
PROCEEDINGS

A SYMPOSIUM ON ADVANCED OXIDATION PROCESSES

FOR THE TREATMENT OF
CONTAMINATED WATER AND AIR

June 4 & 5, 1990
Toronto, Canada

Sponsors:

National Groundwater and Soil Remediation Program (GASReP)

Wastewater Technology Centre of Environment Canada (WTC)

Canadian Association on Water Pollution Research and Control (CAWPRC)

Pollution Control Association of Ontario (PCAO)

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Preface

Chemical contamination of groundwater and industrial wastewaters is an issue of international concern. Unfortunately, commonly used treatment methods are not always effective and some technologies, such as in-situ soil venting and air stripping, create an adverse secondary environmental impact, since the contaminants are simply transferred from water to air.

Advanced Oxidation Processes (AOP's) are promising alternatives for the treatment of hydrocarbons (halogenated and non-halogenated) and other organic chemicals found in contaminated water and in off-gases produced by other treatment technologies.

Given the growing interest in AOP's and the need for interested parties to learn and exchange ideas, the National Groundwater and Soil Remediation Program (GASReP), the Wastewater Technology Centre of Environment Canada (WTC), the Canadian Association on Water Pollution Research and Control (CAWPRC), and the Pollution Control Association of Ontario (PCAO) identified the need for a symposium which would serve as a forum for the exchange of the latest information, ideas, and research results in this important, emerging field.

Specifically, the objectives of the Symposium were defined as follows:

- to identify and discuss state-of-the-art and emerging technologies in the AOP field;
- to examine case studies that have successfully demonstrated, at bench-scale, pilot-scale, and full-scale levels, the use of AOP's for the removal of organics from water and air;
- to discuss current and pending Research, Development and Demonstration (R,D&D) studies.

These **Proceedings** consist of the papers presented at the Symposium. The papers offer a wealth of information on the state-of-the-art of Advanced Oxidation Processes. On behalf of the Symposium sponsors, I would like to thank the speakers for their contributions, and commend them for the quality of the papers that follow.

Dr. Bruce Jank
Director
Wastewater Technology Centre

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For more information about the Symposium or for more copies of the **Proceedings**, please contact

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SESSION 1
THE NEED FOR AOP



**AN INTRODUCTION TO ADVANCED OXIDATION PROCESSES (AOP)
FOR DESTRUCTION OF ORGANICS IN WASTEWATER**

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ABSTRACT:

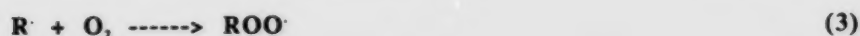
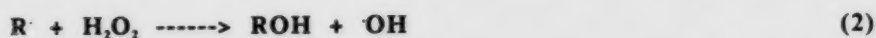
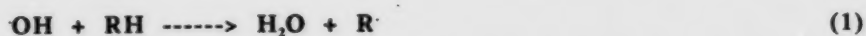
The various processes that have been suggested for the oxidation of organic compounds in wastewater are summarized. The most widely applicable are based on generation of hydroxyl radicals via the photolysis of hydrogen peroxide, ozone and titanium dioxide. Other methods of generating hydroxyl radicals and other oxidants, as well as other methods of oxidation that have been suggested for organic wastewater treatment are also discussed.

INTRODUCTION:

The oxidation of organic pollutants in water is an attractive method of treatment because, if carried to completion, it results in conversion of the organic to innocuous materials such as carbon dioxide and water. Even when the process is not carried to completion, partial oxidation usually results in products with enhanced biodegradability. Unfortunately, the direct reaction of organic compounds with oxygen is, in most cases, too slow to be of practical use. The most effective way of oxidising organics is to use chemical reactants i.e. reactants with a high oxidising potential. The addition of most highly oxidising chemical reagents is generally not considered as a basis for destructive treatment of wastes because such reagents are usually expensive and the addition of large quantities of oxidising agents to a waste solution may result in a new waste treatment problem involving the reduced products of the oxidising agents. For this reason, the potential treatment processes that have received the most attention are those that involve i) additions of energy to initiate oxidations, ii) additions of non-polluting oxidising agents such as hydrogen peroxide and ozone, and iii) in-situ generation of reactive species, primarily the hydroxyl radical. As shown in the following table, the most highly oxidizing species available is the hydroxyl radical (Clarke & Knowles, 1982). For this reason, most advanced oxidation processes (AOP) for waste treatment are based on generation of hydroxyl radicals to initiate oxidations.

Oxidant	Oxidation potential (V)
*****	*****
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate ion	1.67
Chlorine dioxide	1.50
Chlorine	1.36
*****	*****

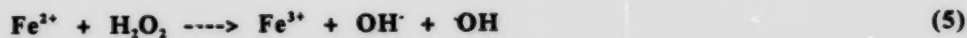
In the presence of organic compounds, hydroxyl radicals react via a number of pathways to generate reactive organic radicals which undergo further reactions usually resulting in oxidation of the organic substrate. A common reaction is the abstraction of a hydrogen atom to initiate a radical chain oxidation



The hydroxyl radical can also add to double bonds in unsaturated and aromatic molecules, again generating partially oxidised radicals capable of becoming involved in radical chain oxidations. There is also some evidence that in the case of halogenated organics, hydroxyl radical attack leads preferentially to replacement of the halogen with OH.

Fenton's Reagent

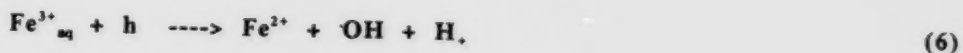
One of the most common ways to generate hydroxyl radicals in the organic chemistry laboratory for the oxidation of organic compounds is Fenton's reagent. This reagent is based on the catalytic effect of ferrous ions on the decomposition of hydrogen peroxide.



The reaction is very efficient in generating hydroxyl radicals but involves consumption of one molecule of Fe^{2+} for each hydroxyl radical produced. Since it is not realistic to expect to add Fe^{2+} to wastewater, Fenton's Reagent has been ignored as a basis for wastewater treatment.

Photochemistry of metal ions and complexes

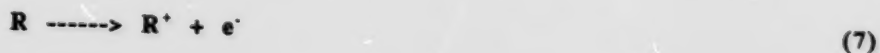
Most metal ions with coordinated water will produce hydroxyl radicals when irradiated at wavelengths of the water-to-metal charge transfer transition. The best studied example is the photolysis of Fe^{3+} .



Although it was recently demonstrated that the mineralization of formaldehyde by hydrogen peroxide could be greatly accelerated by the addition of ferric ion as catalyst (Murphy et al., 1989), a waste treatment process based on the Fenton Reaction has not been given serious consideration. This is likely because the reaction consumes Fe^{3+} and produces Fe^{2+} , and water treated by addition of ferric ion would likely require further treatment to remove iron prior to discharge. For this reason, it is not viewed as a realistic way to generate hydroxyl radicals for water treatment.

Electrochemical oxidation

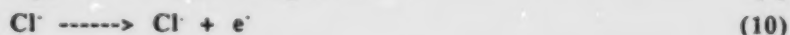
Electrochemists are fond of claiming that every successful chemical oxidation reaction has its electrochemical counterpart. Unlike the chemical oxidation, the electrochemical one involves no additions of chemical oxidants that then have to be removed. Anodic oxidation as a method of destroying organics in effluents has been discussed for some time (Kuhn, 1972). It is generally viewed as a direct technique, ie. it involves the direct transfer of one electron from the organic to the electrode to form a cation radical, although some authors claim indirect oxidations also could be important. In the direct pathway, the fate of the cation radicals governs the products formed. For this reason, most commercial electrochemical oxidations are used for synthesis rather than destruction.



Generally speaking, the technique is impractical because the complete oxidation of organics to carbon dioxide is not a facile reaction and only takes place readily for some species under specific conditions. Even for those species that react, the complete oxidation requires the transfer of many electrons and has a high energy consumption. The power consumed in this process is the main operation cost and is $V \times A$, where V is the voltage of the system and A is the current passing through it. However, a more relevant factor is the current efficiency

$Ax/100$, where x is the percentage of the power used in the desired reactions as opposed to undesired reactions.

In effluents, organic oxidations at high current densities have to compete with the anodic oxidation of water to oxygen and with the oxidation of other components of the solution, for example the formation of chlorine atoms from chloride ions. In general, aromatic compounds have higher oxidation potentials than water and therefore don't effectively compete with solvent reactions.



A number of authors have suggested that the oxidation of anodic oxidation of water produces reactive species such as hydroxyl radicals that can oxidise organics indirectly (Weinberg and Weinberg, 1968), but this is disputed by Kuhn (1972). According to Kuhn (1972) there is very little evidence for the oxidation of organics under conditions of oxygen evolution at anodes. In fact, in most systems studied, usually at constant current density, as the easily oxidised organics are consumed and the voltage increases to keep the current constant, water oxidation becomes increasingly more important at the expense of organic oxidation. A disadvantage not commonly discussed is that the effluent must have a significant conductivity. Most laboratory studies are performed in salt solutions of concentrations of the order of tenths of molar.

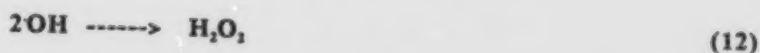
A number of reports of electrochemical oxidation of effluents are reported. None of them involve complete oxidation to carbon dioxide. Ho et al. (1986) studied the effect of electrode material on the electrochemical oxidation of simple sugars. With one electrode, they observed a 98% reduction in COD. The sugars were converted to formaldehyde and formic acid. In the anodic oxidation of phenol, Smith de Sucre and Watkinson (1981) that the rate of reaction was a function of mass transfer to the surface the that the products were more stable and some accumulated in the solution. Several studies on effluents have shown that for electrochemical processes to have acceptable rates of reaction and current efficiencies, a high electrode surface area and high rate of mass transfer to the surface is needed. This is best accomplished through the use of porous electrodes. Pletcher (1982) claims a high surface area cell has been used for the treatment of paper mill effluents achieving a 70% reduction of BOD and a 95% removal of chlorinated phenols.

Photolysis of H_2O_2

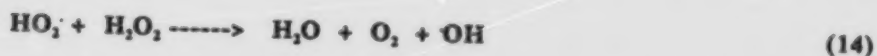
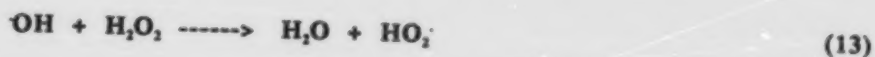
The simplest process available for the generation of the hydroxyl radical, is the **direct photochemical cleavage of hydrogen peroxide**. Early research on the photolytic decomposition of hydrogen peroxide has been summarized by Symons (1962). The quantum yield of this process is very high, approaching the theoretical upper limit of two hydroxyl radicals formed per quantum absorbed.



Although this is conceptually the simplest method of hydroxyl radical production, a number of factors can combine to reduce its efficiency. Since the two radicals are produced in a solvent cage, there is some probability of a radical-radical recombination reaction consuming the two hydroxyl radicals before they can escape the cage. Because of this cage effect, the limiting yield for hydroxyl radicals in solution during the photolysis of H_2O_2 is about 0.5. Even for those radicals escaping the cage, the radical-radical recombination is still an important reaction pathway in the absence of other reactants.



Hydroxyl radicals can also initiate a radical chain decomposition of hydrogen peroxide via the following reactions;



Carbonate and bicarbonate ions also efficiently react with hydroxyl radicals and when these ions are present, they can act as hydroxyl radical scavengers, decreasing the efficiency of any competing oxidations.

A more serious problem involves exceptionally low molar absorptivity of hydrogen peroxide in the readily accessible UV region. For example, the most efficient generation of light in the 200-300 nm region is accomplished using low pressure mercury lamps. These lamps are approximately 30% efficient in converting electrical energy to light energy and about 80% of their emission is at 254 nm. Hydrogen peroxide begins to absorb at wavelengths greater than 400 nm with the spectrum exhibiting a slow steady rise from 400 to 185 nm with no maximum being reached. It is photoreactive over this entire wavelength range. Unfortunately

the molar absorptivity of hydrogen peroxide at 254 nm is only about $20 \text{ M}^{-1}\text{cm}^{-1}$ (Glaze et al., 1987). If we assume that 10^{-4} M is a reasonable peroxide concentration, it would take a path length of 1000 cm for 99% of the light to be absorbed. However, the low pressure mercury lamp operates at relatively low power and a typical application might require from one hundred to several hundred lamps. Separating each lamp from its neighbours by 1000 cm would result in an extremely large reactor. Absorptivity can be increased and therefore the path length required for total absorption decreased by increasing the concentration of hydrogen peroxide. For a more realistic path length of 10 cm, the concentration of hydrogen peroxide needed to achieve 99% absorption would be 10^{-2} M . The absorptivity of hydrogen peroxide at 220 nm is about 5X the absorptivity at 254 nm so there is some advantage to be gained from using lamps with output at lower wavelengths however this increased absorptivity might be balanced by the decreased efficiency of lamps producing these wavelengths.

The low absorptivity of hydrogen peroxide suggests that a system based on direct irradiation of this reactant would be very susceptible to interference from other high levels of suspended solids and other absorbing substances in the water. It should be noted that the possibility exists that if the pollutant absorbs the UV more strongly than the hydrogen peroxide, its excited state may be more reactive towards hydrogen peroxide than ground state organics and oxidations may be initiated via this pathway. In any case, performance of a reactor based on direct irradiation would be strongly dependent on the character of the influent and therefore system design would have to be based on direct testing of the water to be treated.

Despite these limitations, several authors have demonstrated that the process works. Borup and Middlebrooks (1987), using low pressure mercury lamps, reduced concentrations of dimethyl phthalate in distilled water from 50 mg/L to $<0.05 \text{ mg/L}$ by dosing with approximately 125 mg/L hydrogen peroxide and irradiating with an intensity of 1210 microwatts/cm² for 60 min. Isophorone concentrations of 60 mg/L could be reduced to $<0.05 \text{ mg/L}$ by dosing with 250 mg/L and the same irradiation conditions. In their study of the destruction of benzene using $\text{H}_2\text{O}_2/\text{UV}$, Weir et al. (1987) quote several studies involving the use of this technology to treat TNT-containing waters, remove TOC from tap and boiler feedwater, oxidize acetate in shipboard waste and oxidise trichloroethylene.

Photolysis of ozone

The chemistry of ozone in solution involves a potentially bewildering array of reactions, particularly when other factors such as UV and H_2O_2 are included. They are best understood by first attempting to understand the normal chemistry of ozone and then considering

reactions with organic and inorganic substrates and finally the effect of light on these reactions. The decomposition kinetics of ozone have been described in detail by Staehelin and Hoigne (1985).

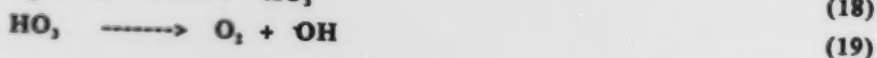
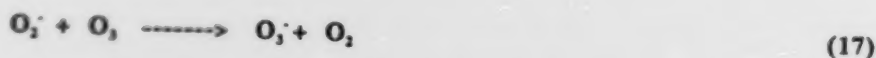
In neutral solution, ozone is unstable and decomposes via a series of chain reactions. The reaction sequence is usually initiated by a hydroxyl radical attacking an ozone molecule to form oxygen and a hydroperoxyl radical



In neutral solution, the hydroperoxyl radical deprotonates ($\text{pK}_a = 4.8$) to its conjugate base, the superoxide radical anion



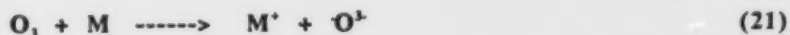
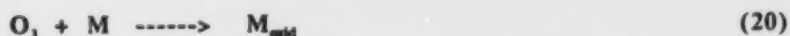
The superoxide formed in reaction (16) then goes on to react with a second molecule of ozone to via a three step reaction sequence that ultimately results in two molecules of oxygen and a new



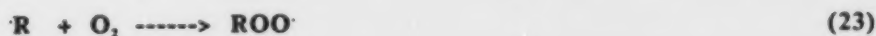
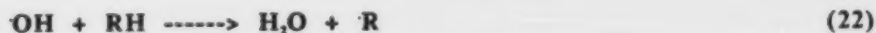
hydroxyl radical that can react with another ozone molecule as in reaction (15) and start the chain over again. The net effect of these reactions is to keep a low concentration of hydroxyl radicals around in solution at the expense of ozone, the concentration of which continually decreases unless further additions are made. The half-life of ozone in distilled water at pH 7 is on the order of 10^3 sec. Molecules that react with hydroxyl radicals interrupt the chain decomposition and increase the half-life of ozone. As mentioned above, carbonate is an efficient scavenger of hydroxyl radicals. In the presence of 2M HCO_3^- the half-life of ozone increases to 10^4 sec.

In basic solution, hydroxide ions react with ozone to produce one superoxide ion and one hydroperoxyl radical. The hydroperoxyl radical rapidly deprotonates via reaction (16) to give another superoxide ion. Each of these superoxide ions reacts with a molecule of ozone to produce hydroxyl radicals via reactions (17) - (19).

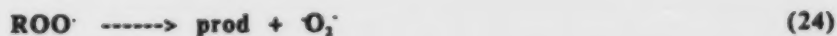
In view of the complexity of ozone decomposition kinetics, it is hardly surprising that ozone can react with organic substrates via a number of different pathways. The simplest pathway is the direct reaction of ozone with the organic. In some cases, this direct reaction results in the production of an ozonide ion, O_3^- which then produces a hydroxyl radical via reactions (18) & (19), whereas in other cases, organic ozonides or other oxygenation products are formed.



In terms of organic degradation, the most important reaction is probably the reaction between the organic and the hydroxyl radicals produced in reaction (15). A general reaction sequence for these substances is



In some cases, eg oxidation of alkyl groups or addition of hydroxyl radicals to aromatics, this reaction terminates the chain because the resulting radicals do not produce species that interact with ozone. However, in other cases, the resulting organic peroxy radicals can undergo a base catalysed reaction that produces the superoxide radical anion, which reacts with another molecule of ozone to produce a hydroxyl radical via reactions (17) to (19).



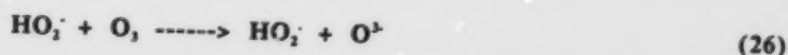
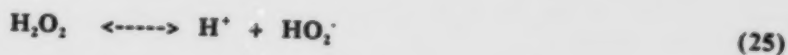
The rate at which an organic substrate will be oxidized in an ozone reactor will depend on two factors: (i) the bulk ozone concentration available at any given time; and (ii) the overall reactivity of the substrate towards molecular ozone and OH . The bulk ozone concentration will be controlled by factors such as the rate of mass transfer into the solution, pH and chemical composition of the water, the presence of initiators of the radical chain decomposition (ie. by the rate of ozone supply and spontaneous decomposition). Many molecules react very slowly with molecular ozone so in these cases, the rate of oxidation of organics will depend on the rate of hydroxyl radical formation. In general, higher ozone concentrations will result in faster rates of organic oxidation. However, higher ozone concentrations will also decrease the efficiency of the reaction with respect to ozone. This is because the efficiency of the oxidation of organics with ozone depends on the effectiveness of the organic substrate at trapping hydroxyl radicals in competition with reaction (15), the reaction between hydroxyl

radicals and ozone. In the simplest case, that where reaction (24) doesn't occur, the efficiency is given by the expression

$$k_{22} [\cdot\text{OH}][\text{org}] / (k_{22} [\cdot\text{OH}][\text{org}] + k_{15} [\cdot\text{OH}][\text{O}_3])$$

Glaze et al. (1987) claim that in the $\text{H}_2\text{O}_2/\text{O}_3$ destruction of trichloroethane in the presence of 300 mg/L bicarbonate ion, only 4% of the ozone transferred is utilized for the destruction of 90% of 600 ug/L TCE. These factors are important because the most expensive part of ozone based systems is the ozone generator and operating costs associated with ozone generation.

Hydrogen peroxide can also become involved in these reactions. Several authors have shown that the conjugate base of H_2O_2 can initiate the decomposition of ozone by the reactions



The HO_2 goes on to react with ozone and produce hydroxyl a hydroxyl radical via reactions (16) to (19). Since $\cdot\text{OH}$ promoters such as H_2O_2 and O_2^- are produced during the oxidation process, it is likely that the radical pathway for oxidation of organics becomes more important as the reaction proceeds.

Although many authors have shown that the presence of UV light can accelerate the oxidation of some substrates by ozone, the actual mechanism of the catalysis has not been demonstrated. Most of the authors have assumed that the photolysis of ozone in solution produces $\cdot\text{OH}$ since the photolysis of ozone in wet air is known to produce this radical. The process in wet air seems to be



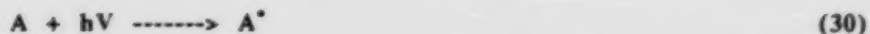
However, in solution it is generally felt that the two hydroxyl radicals are prevented from escaping the solvent cage without combination. The net product is hydrogen peroxide. The amount of free hydroxyl radicals produced in the solution phase photolysis of ozone has apparently not been measured. The overall photolysis of ozone in solution is therefore likely

to be represented by reaction (29)



Since hydrogen peroxide is a promoter of hydroxyl radical formation via the reactions described above, it may be that uv/ozone is just an expensive way to produce the ozone decomposition initiator hydrogen peroxide. In this case, direct addition of hydrogen peroxide makes more sense.

Another possible mechanism for a catalysis of the oxidation of organics with ozone is enhanced reactivity of molecular ozone with excited states of the organic substrate. In this case, the light is absorbed by the organic to produce an excited state



The excited state, A^* , then reacts with molecular ozone via reaction (31)



In order for this reaction to be important, the excited state must live long enough to encounter a molecule of ozone and the reactivity of the excited state must be significantly greater than the reactivity of the ground state towards ozone. The rate of this reaction will be directly related to the amount of light absorbed by the substrate per unit time. Since the excited state will both radiationless and radiative deactivation processes if it doesn't react,



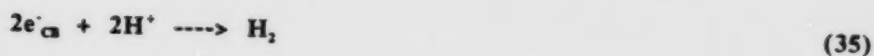
the efficiency of the excited state pathway will be related to

$$k_{31}[\text{A}^*][\text{O}_3]/(k_{31}[\text{A}^*][\text{O}_3] + k_{32}[\text{A}^*])$$

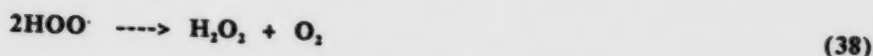
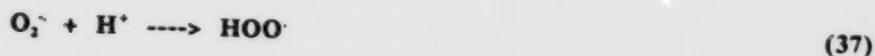
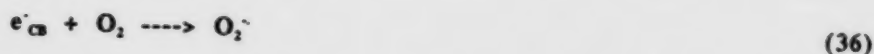
Thus the efficiency of this reaction will be enhanced by high concentrations of ozone. Unfortunately, ozone itself absorbs light. If it competes with the organic for the irradiation wavelengths, high concentrations of ozone will result in less light being absorbed by the organic and therefore, reduced rates of reaction.

Heterogeneous photocatalytic decomposition of water

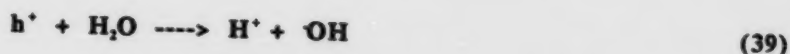
This process is based on the photochemical production of an electron-hole pair in a solid semiconductor under irradiation by light of energy greater than its optical bandgap. The electron and the hole migrate to the solid-solution interface where they can react with species in solution. Transfer of electrons across the interface is dependent on the relative energy levels of the hole and electron traps on the solid surface and of the energy levels of electron donors and acceptors in the solution (for recent reviews, see Gerischer, 1985 and Gratzel, 1989). Although much of the early interest in heterogeneous photolysis was due to the possibility of hydrogen production due to the reaction of conduction band electrons with hydrogen ions,



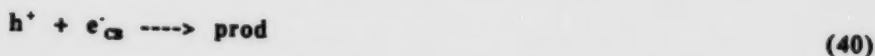
the most common electron acceptor in solution is molecular oxygen. The superoxide ions produced via reaction (36) readily protonate and disproportionate according to reactions (37) and (38) to give hydrogen peroxide and oxygen.



If the energy levels are right, the valence band holes can react with water at the interface to produce hydroxyl radicals via



The efficiency of this process is governed by the rate of the back reaction (40)



Because the rate of reaction is equal to $k_{40}[h^+][e^-_{cb}]$, both holes and electrons need to be scavenged efficiently in order that neither build up until the back reaction predominates.

There is experimental evidence to indicate that when the hydroxyl radical is produced, it remains adsorbed at the interface. Thus in order for it to react with organics, they probably also need to be adsorbed or very near the surface at the time of excitation. For very dilute solutions, the rate of reaction is very likely limited by the rate of mass transfer of the substrate to the surface.

Nearly all the proposed applications of this technique involve the use of the anatase phase of titanium dioxide as semiconductor. This compound is stable under a variety of conditions, and is more efficient at oxidising organics than a variety of other semiconductors (Carey and Oliver, 1980), presumably because it has the necessary energy level positions to produce hydroxyl radicals.

Since the use of TiO_2 was first suggested as a photocatalyst for the treatment of wastewater, based on studies of the disappearance of PCBs in the presence of TiO_2 suspensions (Carey et al., 1976), it has received a great deal of attention. The degradation of a large number of organics in illuminated TiO_2 suspensions has been demonstrated, many of them completely mineralized (for a recent review, see Ollis et al., 1989). Reactive substrates include chlorophenols, chlorobenzenes, PCBs, 2,4,5-T, chloroalkanes, chloroacetic acids and a dichlorodioxin.

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THE CANADIAN ENVIRONMENTAL PROTECTION ACT
AND
THE FISHERIES ACT:
THE REGULATORY AGENDA

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ABSTRACT

The Canadian Environmental Protection Act is comprehensive legislation dealing with toxic substances. Under it, substances already in use in Canada and substances new to Canada can be controlled. One of Canada's oldest pieces of legislation, the Fisheries Act, is also used to protect the environment. Regulations under it are now being re-written. Environmental protection legislation in Canada will be enforced; CEPA's promulgation was accompanied by the release of a stringent enforcement and compliance policy.

INTRODUCTION

Thank you. I am pleased to have the opportunity to be with you today to discuss the federal government's approach to environmental protection, in particular, how we are dealing with the problems associated with the use of toxic substances.

I intend to concentrate on three areas:

- 1) The Canadian Environmental Protection Act. I would like to provide you with an understanding of its legislative framework, the range for regulatory intervention and our regulatory agenda to control the more insidious toxic releases.

- 2) I will also speak to you about one of Canada's oldest pieces of legislation - the Fisheries Act and its provisions to protect fish habitat.
- 3) As well, I will comment on the enforcement and compliance provisions under CEPA and the federal government's commitment to ensure that federal environmental protection laws are upheld.

Over the last few years, public opinion polls have consistently shown that, for Canadians, the protection of the environment is a priority issue. Even though great tracts of the country do not show the obvious and more overt signs of environmental degradation, those of us living in the industrialized south do not have to look far to see what our modern world has wrought. Over the last few years, there has been a growing realization that comprehensive new environmental legislation aimed directly at the major source of the problem, toxic substances, was needed.

In 1982, the Canadian government began to consider strengthening the legislative basis for environmental protection. We met with provincial and municipal governments, with industry, with labour, with the academic community and with public interest groups. We solicited advice from members of the public in regional and national meetings.

After this extensive consultation process, a consensus of views emerged that the protection of the environment is essential to the very well-being of Canada as a nation. In particular, we recognized the need to rationalize and strengthen the management of toxic substances at all stages of their life cycles - from manufacture through transportation, use and storage, to disposal.

Out of this consensus new legislation emerged: the Canadian Environmental Protection Act, (CEPA) for short. CEPA became law on June 30, 1988. The Act builds on earlier environmental statutes such as the Clean Air Act, the Ocean Dumping Control Act and the Environmental Contaminants Act.

The opening declaration of the Act states that "the protection of the environment is essential to the well-being of Canada". The new legislation embodies a multi-media approach to environmental protection. It focuses directly on pollution problems on land, in water, oceans and through all layers of the atmosphere. CEPA gives the federal government broad powers to define national standards for any substance that threatens to harm the health and/or environment of Canada and its citizens. The objective of the statute is to anticipate and

prevent any environmental contamination that would threaten human health and the environment.

The Act deals with organic and inorganic substances, the products of biotechnology, emissions, effluents and wastes. It gives government the authority to impose strict controls at each stage of a substance's or a product's life cycle.

The Act is designed to protect against toxic contamination. Under CEPA, a substance is toxic if it threatens human health, or the environment itself - plants and wildlife. The Act adopts a two-pronged approach to managing toxic substances.

- 1) CEPA enables the government to tackle those substances now in the Canadian marketplace, many of which we know little about; this is very much an after-the-fact, catch-up approach to environmental protection - one that now confronts all industrialized nations.
- 2) More importantly, the Act stringently controls the introduction of substances new to Canada. This preventative approach should ensure that we do not repeat the mistakes of the past.

In terms of the first approach, managing toxic substances already in use in Canada, CEPA creates a list of priority substances identifying those which most urgently need assessment for their health and environmental impacts. The list was compiled from nominations submitted by individuals representing different sectors - labour, industry, governments and public interest groups. There are 44 substances on the Priority Substances List and, under CEPA, the government must complete an assessment of each substance within 5 years. Based on the results of those assessments, regulatory controls will be established for particular substances at those points in their life cycle where releases can occur.

The Priority Substances List includes substances such as benzene, dioxins, waste crankcase oils, cadmium, chromium, toluene and methyl tertiary-butyl ether. Regulations have already been introduced for substances as varied as ozone layer depleting chlorofluorocarbons and PCBs. Public consultations are under way on proposed regulations to control chlorinated dioxin and furan releases in pulp and papermills' effluents.

CEPA's second approach to managing toxic substances deals with substances new to Canada, either through importation or manufacture. The notification system for new substances requires that importers and manufacturers submit data necessary to complete an assessment

of the particular substance prior to its introduction into Canada. The data required include the physical, chemical and biological properties of the substance in question, exposure data for those handling or working with the substance, effects on animals, effects on the environment including bioaccumulation, toxic effects on populations in the ecosystem, and so on.

CEPA reflects the political realities that make up our confederation. The Canadian constitution divides legislative powers between the ten provinces and the federal government. As a general rule, the federal government has responsibility for issues that are transboundary, involving one or more provinces, and for ensuring peace, order and good government. The Canadian provinces have jurisdiction over land and natural resources south of the Arctic regions. They have a great deal of responsibility for the environment and use legislative and regulatory instruments to carry out that responsibility.

The Canadian Environmental Protection Act provides a national focus for environmental protection initiatives. Efforts to manage toxic substances will be maximized through equivalency agreements with the provinces. Under CEPA, the federal government will recognize the application of provincial regulations if they are comparable in effect. In this way the provincial government is given the option of developing and using its own statutes for regulating.

Administrative flexibility of this type is an advantage in Canada's federal system. Such agreements, for instance, ensure that industry is spared the double jeopardy of competing federal and provincial regulations.

The Fisheries Act is one of Canada's oldest pieces of legislation. The Act was promulgated in 1868, one year after confederation, and then, as now, the Fisheries Act contained provisions prohibiting the pollution of fish-bearing waters. A number of court cases in the late 19th century and early 20th determined that the federal government had jurisdiction over all aspects of fisheries management in coastal waters, as well as inland waters, even though actual property rights for fish in inland waters reside with the provinces.

Environment Canada is primarily responsible for Section 36 of the Fisheries Act. Subsection 36(3) is the cornerstone of the pollution provisions of the Act; it prohibits the deposit of substances deleterious to fish or fish habitat.

Between 1971 and 1977, 6 industrial effluent regulations were promulgated. These regulations specify and authorize the deposit of certain amounts or concentrations of deleterious substances from the following operations:

- Chlor-alkali Mercury Plants
- Pulp and Paper Mills
- Petroleum Refineries
- Base Metal Mines
- Meat and Poultry Plants
- Potato Processing Plants

More stringent Pulp and Paper Effluent Regulations under the Fisheries Act have been developed and will come into force on January 1, 1991. The regulations for base metal mines will also be strengthened during 1991.

Upwards of 64 new regulations under the Canadian Environmental Protection Act and the Fisheries Act will be introduced over the next three years. Substances such as polycyclic aromatic hydrocarbons (PAHs), creosote-impregnated waste materials and inorganic fluorides are among those likely to be regulated. This comprehensive environmental regulatory agenda will go a long way to protecting Canadians from the presence of toxic substances in the environment.

Enforcement is a vital component of the Canadian Environmental Protection Act. Promulgation of the Act was accompanied by the release of a comprehensive enforcement and compliance policy. A program of inspections, complemented by spot checks, is in place to verify compliance with the Act and its regulations. When non-compliance is found, violators are subject to a hierarchy of enforcement responses; Warnings, Directions, Ticketing and Prosecutions. The ticketing regulations are not yet in force. The particular enforcement response depends on:

- 1) the nature of the violation;
- 2) the effectiveness of achieving compliance with the Act within the shortest possible timeframe; and
- 3) the likelihood of no further occurrence of the violation.

The Act includes significant penalties, ranging from fines of \$200,000 and six months in jail to fines of \$1,000,000 and three to five years in jail. For offences involving criminal negligence, life imprisonment is possible. In 1988 -1989, Environment Canada officials conducted over 5000 inspections or investigations. As new regulations come on line, increased resources for enforcement activities are being deployed.

An Enforcement and Compliance Policy is also being developed for the Fisheries Act.

Deterrence is the ultimate goal of environmental enforcement - the true measure of success would be a 100% compliance rate for all environmental protection regulations.

Environmental issues, over the last few years, have been at the forefront of the public agenda. There is no reason to suspect that this is going to change. A strong regulatory framework to ensure environmental protection will continue throughout the decade. The new Canadian Environmental Protection Act, by virtue of its comprehensive nature and its flexibility, is the right tool for the times. The Act can afford the protection the nation demands.

**ENVIRONMENTAL PROTECTION AGENCY
WASTEWATER DISINFECTION POLICY:
BALANCING PUBLIC HEALTH AND AQUATIC LIFE RISKS**

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ABSTRACT:

In late 1988, the Office of Water of the U.S. Environmental Protection Agency decided to reconsider its policy on municipal wastewater disinfection in view of the increasing trends among the states to restrict the discharge of total residual chlorine to the Nation's waterways. A Task Force was formed to examine the policy that had been in place since July 1976 and update it, if necessary, to account for the technological and institutional changes that had taken place in that time period. This paper summarizes the findings of the Task Force and discusses how the policy has not substantially changed from one that has existed since 1976.

INTRODUCTION

One of the major goals of the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) was to achieve a level of water quality that "provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water". This was known as the "fishable and swimmable" goal of PL 92-500. In practice, the application of this goal brought about a regulatory dilemma that still pervades the field today. The dilemma arises from the extensive use of chlorine for wastewater disinfection, because chlorine, the disinfectant still used in most POTWs for pathogen control, is itself toxic to fish and other aquatic life and therefore a pollutant that must be controlled and regulated. While chlorination of municipal wastewater discharges has contributed to the reduction or elimination of many waterborne diseases, chlorine residuals and by-products may cause adverse impacts to aquatic life when discharged to the environment.

The toxicity of chlorine residuals in wastewater was recognized many years ago and has since been extensively documented.^{1,2} The harmful effects to aquatic life from chlorinated wastewater have been demonstrated even at extremely low levels of chlorine residual.³ These effects are both acute and chronic. While some organisms are able to avoid the toxicity of chlorinated wastewater plumes, avoidance can result in changes in behavior patterns, increased stress on aquatic ecosystems, and loss of habitat.^{4, 5}

The harmful impacts to aquatic life from chlorine residuals are potentially extensive because the practice of wastewater chlorination is so widespread. Yet the harmful effects of wastewater chlorine residuals, and to some extent by-products, would seem to be easy to reduce relative to the effects caused by many other toxic substances in wastewater. The sources of chlorine residuals and by-products in wastewater discharged to the Nation's waters are identifiable and readily controlled. Discharges of chlorine residuals and, in some cases, by-products can be reduced by changing disinfection technologies, modifying operating procedures, and reducing or eliminating disinfection requirements. The difficulty lies in achieving the appropriate balance between protection of public health and protection of aquatic life without imposing undue economic burden on the discharges.

A joint State and EPA Task Force was formed in 1988 to review EPA's existing municipal wastewater disinfection policy and revise it if necessary to assure an appropriate balance between protection of public health and aquatic life. The Task Force developed a statement of policy and supporting documentation. This paper discusses the development of the updated policy and summarizes the Task Force report supporting the policy.

HISTORY OF EPA'S DISINFECTION POLICY

Prior to the passage of PL 92-500 in 1972, wastewater disinfection was primarily a state responsibility. As a result, disinfection requirements and practices varied markedly from state to state. When the initial regulatory definition of secondary treatment (FR, August 17, 1972, p. 22298) was established in response to PL 92-500 as the basis for setting municipal effluent discharge limitations, it stated that the 30-day geometric means of effluent fecal coliform bacteria shall not exceed 200/100 mL. The fecal coliform limitation amounted to a nearly universal disinfection requirement which, for reasons of cost and effectiveness at reducing fecal coliforms, encouraged the widespread practice of chlorination.

Based on the recommendations of an earlier EPA Task Force⁶ that reviewed the wastewater disinfection issue, EPA amended the secondary treatment regulation in 1976 to eliminate the fecal coliform limitation. The notice of that rule change (FR, July 26, 1976, p. 30786) stated that although protection of public health would continue to be the overriding decision criterion, the Agency believed that the objective could be achieved without universal and continuous disinfection. The 1976 rule noted that disinfection was not mandatory and exceptions could be made on a case-by-case basis. Disinfection requirements were to be established in accordance with state water quality standards, and would continue to be enforceable conditions of NPDES permits. Where disinfection was found to be necessary and protection of aquatic life was a priority, the cost of chlorination and dechlorination was to be compared to alternatives, (e.g., ozone, bromine chloride, and ultraviolet light).

After the 1976 changes, the debate over public health protection vs. aquatic life protection was argued often in public forums. In the mid-1980's three events occurred that stimulated EPA's Office of Water to re-examine the disinfection policy. In 1984, EPA issued recommended limits for exposure of aquatic organisms to chlorine². In 1986, EPA recommended *Escherichia coli* and enterococci rather than fecal coliforms as the preferred indicators for use in setting recreational water quality criteria.⁷ An EPA study the following year⁸, which examined chlorination practices at 6,300 municipal wastewater treatment plants discharging to freshwater streams, concluded that about two-thirds of those discharges are likely to contribute to exceedances of EPA's acute aquatic life criteria for chlorine. The study also noted that many states had not adopted chlorine criteria or incorporated them into water quality standards.

This study sparked renewed Agency interest in the wastewater chlorination issue. As a result, the new Municipal Wastewater Disinfection Task Force was formed to consider new information which has become available since 1976, and to update EPA's policy if necessary.

The Task Force considered four key issues before making its final recommendations: protection of public health, protection of aquatic life, reducing disinfection requirements, and institutional impediments to policy modification.

PROTECTION OF PUBLIC HEALTH

EPA's disinfection policy seeks to provide an appropriate balance between protection of public health and protection of aquatic life. The proposed policy shifts disinfection practices towards reduction or elimination of disinfection where feasible while still protecting public

health. To provide background for this recommendation, the Task Force reviewed data relevant to the health consequences of disinfection: What is the public health risk associated with pathogens in wastewater? Does disinfection effectively reduce this risk? Does disinfection have any negative health impacts?

Available data indicate an association between swimming-related gastrointestinal illness and the quality of bathing waters.^{9,10} Several studies have shown that disinfection effectively reduces the number of pathogens in wastewater.¹¹ Together, these studies suggest that wastewater disinfection does help to protect human health from recreational exposure to pathogens. Several risk assessments^{4,9,10} indicate that ceasing wastewater disinfection may lead to unacceptable risks from exposure to pathogens in recreational waters. Inefficient or interrupted treatment of drinking water coupled with poor water quality has caused several thousand cases of waterborne illness in the U.S.¹¹ Thus it appears that wastewater disinfection may be valuable in certain circumstances as an additional safeguard for consumers of drinking water.

The Task Force evaluated the extent to which the by-products of wastewater chlorination, such as trihalomethanes, pose a threat to public health. They acknowledge that data are limited, but agreed that, because these compounds are formed at low levels, they do not appear to represent a threat to public health. There is a need, however, for additional basic research on these compounds.

After reviewing the available data, the Task Force concluded that disinfection practices must maintain an adequate level of public health protection, and that protection of public health must remain the overriding criterion in decisions about disinfection requirements.

An outgrowth or extension of the public health protection issue is the indicator organism question. The use of *E. coli* and enterococci as substitutes for fecal coliforms is somewhat controversial for several reasons. In particular, some data call into question whether enterococci are a more conservative indicator than fecal coliforms. The Task Force considered the many issues associated with these organisms. Despite reservations expressed by some states, the Task Force concluded that the new indicator organisms can more accurately determine risks associated with contaminated waters than can fecal coliform measures. However, further research may be needed to determine the appropriateness of these indicators in certain situations.

PROTECTION OF AQUATIC LIFE

The ecological implications of wastewater chlorination are not fully understood. Numerous field and laboratory studies conclusively demonstrate that total residual chlorine is acutely toxic to aquatic life at low concentrations. Toxicity of TRC can range from avoidance of a chlorine plume by fish, to alterations in fish diversity and density, to death, and the toxicity varies according to species.⁴ However, some in-stream studies suggest that residual chlorine does not cause significant aquatic life impacts, particularly if exposure is relatively brief.^{5,12}

Less is known about the chronic aquatic toxicity of chlorine; in the past few years, some in-stream studies have been conducted that confirm laboratory studies of significant chlorine toxicity. Areas of concern include nonlethal effects such as behavioral changes and bioaccumulation, both of which can disrupt the food chain. Aquatic plants appear to be less sensitive to chlorine than fish and invertebrates. Data on the aquatic toxicity of chlorination by-products are limited. However, some studies show that levels of these by-products in effluents are below levels known to be acutely toxic to aquatic life.⁴

Based on reviews of the scientific data available since 1976, the Task Force concluded that total residual chlorine is toxic to aquatic life at the low concentrations produced at wastewater treatment plants, and that TRC levels from these sources should be reduced. However, they stated that more information is needed on the actual instream risks, particularly chronic effects, in order to better understand the impacts that chlorine and other disinfectants have on aquatic life. More data are also needed on the effects of chlorination by-products on aquatic life. The Task Force recommended that more emphasis be placed on aquatic life protection wherever disinfection is practiced. They concluded that numeric chlorine water quality standards developed by the states, based on EPA criteria or site-specific criteria, will protect aquatic life from adverse impacts due to unacceptable levels of chlorine toxicity; however, less than half the states thus far have adopted such criteria.

REDUCING DISINFECTION

The Task Force examined situations where reduced disinfection may be appropriate. These include situations in which the chance of human contact is remote; where excessive chlorination is taking place; or where water quality standards are exceeded. Elimination of disinfection should also be considered where primary and/or secondary contact use is unattainable or where primary and/or secondary contact recreation is unlikely to occur (and there is no downstream public water system intake). The Task Force reaffirmed the need for disinfecting wastewater for primary contact recreation and raised the possibility of reducing disinfection for secondary recreational water uses.

The Task Force identified several ways in which disinfection can be reduced. These include seasonal disinfection, lower levels of disinfection, elimination of disinfection where appropriate, improvements in the efficiency of chlorination, technological modifications to the treatment process, and the use of alternative treatment technologies.

SEASONAL DISINFECTION

In areas of the country where cold weather limits recreation, seasonal disinfection may be appropriate in some situations. However, there are some concerns associated with seasonal disinfection. One is the potential of sediments to harbor microorganisms during non-disinfection periods.¹³⁻¹⁶

If pathogens are released during the warmer months, the level of protection afforded by seasonal disinfection will be substantially diminished. There is also uncertainty regarding the appropriate intervals for seasonal disinfection that would provide protection against such effects. Another concern is that there may be some risk to people who participate in recreational exposure in colder months. Where states decide to undertake seasonal disinfection,

standard and permit programs may present an obstacle if seasonal disinfection is not already in place (see below). Water quality standards may need to be reexamined if seasonal disinfection is to be a viable option in these situations.

USE OF ALTERNATIVE TREATMENT TECHNOLOGIES

Several technologies offer an alternative approach to wastewater disinfection, including dechlorination, ultraviolet radiation, ozonation, bromine chloride, and chlorine dioxide. The Task Force considered several factors that influence the selection an alternative treatment technology, including effects on aquatic life, public health impacts, safety, and cost. They concluded that dechlorination, while cost-effective and easily retrofitted to chlorination systems, may not remove all potential toxicity. Also, even an infrequent failure of a dechlorination system that allowed chlorine to enter the receiving water could substantially reduce the protection provided. Alternative disinfection technologies such as ultraviolet light and ozone appear to provide adequate disinfection while presenting minimal risks to aquatic life. These technologies have become viable both technologically and economically. Other technologies such as bromine chloride and chlorine dioxide show potential but are less well developed. A comparative cost data base should be developed to facilitate consideration of the various alternative technologies.

INSTITUTIONAL ISSUES

In developing a workable disinfection policy, the ability to implement provisions of the policy is an important consideration. There are currently two institutional issues that could hamper efforts to reduce disinfection: the antibacksliding requirement and the antidegradation policy.

The antibacksliding requirement stems from Sections 303(d)(4) and 402(o) of the Clean Water Act which prohibit modifications to permits that would make them less stringent. The antidegradation policy concerns an institutional framework that makes it difficult to change the "designated use" of a water body. Under the system that has evolved to implement the "fishable/swimmable goal" of the Clean Water Act, each water body is assigned a "designated use" which is believed to be the highest use attainable and desirable for that water body. Standards are set to protect these designated uses. States can modify a designated use only through a formal process called a Use Attainability Analysis. This antidegradation policy would make it difficult for states to "downgrade" the designated use in order to set less stringent standards.

These institutional provisions appear to pose many obstacles to easing disinfection requirements. For example, changing an existing year-round disinfection requirement to seasonal disinfection would probably be prohibited by the antibacksliding requirement, although newly issued permits could have seasonal limits. Also, although many water bodies that have been assigned a primary use designation (e.g., for swimming) may not actually be used for direct body contact, it is difficult to change the designated use. Conducting Use Attainability Analyses for a large number of water bodies would be infeasible, and use modifications for even a few water bodies might be considered too time-consuming by many states.

The Task Force concluded that current environmental policies may present obstacles to reducing disinfection. Requirements for water quality standards and NPDES permits that prohibit modifying use designations or discharge levels may result in excessive and unnecessary use of chlorine. If reducing disinfection is to be considered as a policy recommendation, these institutional issues need to be resolved before any such changes could be implemented. While some minor changes to ease disinfection requirements may be feasible, extensive changes would probably require modification of current standards and permitting policies.

DESIGNATED USES

There are no standardized definitions of the terms "primary" and "secondary" to designate recreational uses of water bodies. Generally, primary use refers to whole body contact, such as swimming, and secondary use defines all other recreational water uses, such as wading and boating, where there may be body contact but ingestion is unlikely.

Secondary use recreation generally requires a lower level of disinfection. The Task Force suggested that secondary use designations be more clearly defined, microbiological criteria for secondary recreational uses be developed, and recreational water uses be subdivided into more categories, with corresponding criteria. This would allow greater flexibility in setting disinfection requirements and prevent unnecessary disinfection.

The appropriateness of the primary use designation for some water bodies was questioned. That is, it is unlikely that some "primary use" water bodies are actually used for swimming, due to their location or shallow depth, or due to the time of year. Thus, some wastewater effluents are overdisinfected relative to their receiving water body's actual (as opposed to designated) use. If the designated use of these waters was modified to secondary use or seasonal use (e.g., primary in summer, secondary in winter), then unnecessary disinfection would be reduced. However, as mentioned above, the antidegradation policy and the anti-backsliding provisions in NPDES permits prohibit such modifications.

TASK FORCE RECOMMENDATIONS

The joint State and EPA Task Force concluded that the Agency should continue to promote elimination or reduction of chlorine toxicity to protect aquatic life, while maintaining adequate protection of public health. The Agency should promote adoption of state water quality standards for chlorine and bacteria which will result in more efficient and appropriate disinfection practices. The Task Force does not recommend significant easing of disinfection requirements until more risk information is available and until institutional obstacles to reduced disinfection are cleared.

POLICY STATEMENT

The basis of EPA's municipal wastewater disinfection policy has not changed significantly. Protection of public health remains the overriding criterion in making decisions about

disinfection requirements. However, greater emphasis is being placed on disinfection practices that protect aquatic life from adverse impacts of wastewater disinfection residuals and by-products, particularly from chlorination. This higher level of aquatic life protection would be achieved through both technological and institutional changes. These changes include reduction or elimination of disinfection where it is possible to do so without adversely affecting public health, greater use of seasonal disinfection, technological and operational improvements to reduce the practice of disinfection in accord with the need and enhance disinfection efficiency, and more extensive use of alternative disinfectants and dechlorination after chlorination.

Reduction or elimination of disinfection requirements is recommended only on a limited basis. Before broader changes can be technically supported and implemented, additional information is needed to better understand the public health and aquatic life risks of modifying disinfection practices. Guidance is also needed to assist states with evaluating those risks. Institutional changes to water quality standards and permitting practices may be needed before reduction or elimination of wastewater disinfection can be extensively implemented.

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**TECHNOLOGY EVALUATION: ADVANCED OXIDATION PROCESSES
VS. CONVENTIONAL TREATMENT TECHNOLOGIES FOR
AQUEOUS CONTAMINANTS**

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ABSTRACT:

Recent technology developments and growing experience with full-scale application of advanced oxidation processes (AOP) have brought this technology to the stage at which it may, in some cases, provide a technically effective, economical alternative to the more commonly used methods of industrial wastewater and contaminated groundwater treatment. Advanced oxidation processes can be technically viable, reliable, and economical in many applications, supplanting more traditional technologies such as carbon absorption and air stripping. Depending on the site specific characteristics and regulatory constraints, AOP may indeed be the superior solution because of its destructive nature. However, as with any technology, careful attention must be given during the technology selection process to its appropriate use and application. Many factors must be evaluated and compared to other potentially applicable technologies during this screening analysis.

CH2M Hill has evaluated and tested several processes, and has been involved with several full-scale applications. Results and performance have varied, and are uniquely specific to each application. This paper addresses the pertinent technical, economic, and practical issues in selecting the AOP process for application, and suggests some specific technology screening criteria which may be applicable to future wastewater and groundwater treatment applications.

INTRODUCTION:

CH2M Hill has evaluated advanced oxidation process (AOP) for industrial wastewater, drinking water and groundwater treatment applications, and has gained substantial experience

with AOP technology. This work has included technology screening and evaluation against numerous comparable technologies. In many cases, bench-scale testing and pilot demonstrations have been performed. One full-scale application was started up one year ago, and a second full-scale application is currently in the detailed design and construction phase. In each of these projects, AOP was evaluated against other potentially feasible technologies. AOP was selected or rejected during the initial technology screening phases based on system performance requirements, and its applicability for the specific operating conditions.

Although AOP may be an effective and economical choice in many circumstances, many factors, both technical and practical, must be taken into consideration prior to selecting AOP for treatment of industrial wastewater, contaminated drinking water, or groundwater. Technologies commonly evaluated against AOP for treatment of organic constituents in groundwater and industrial wastewater include:

- Granular Activated Carbon
- Air Stripping
- Biological - Aerobic Activated Sludge, Fixed-Film, etc.
- Wet Air Oxidation
- Other Chemical Oxidation Methods - Sodium Hypochlorite, Hydrogen Peroxide, Ozone, Chlorine Dioxide, Potassium Permanganate, etc.

It is the engineer's responsibility to carefully evaluate all potentially applicable technologies during the initial assessment and screening phases of any industrial wastewater treatment or groundwater remediation project. The following discussion addresses the specific applicability of AOP, and circumstances under which this technology can best be applied. Case histories where AOP was selected or rejected based on technology screening and treatability testing are also presented.

PROJECT DEFINITION

Prior to selecting the best available treatment technology for a specific application, one must understand the specific conditions governing the project implementation. Many considerations, both technical and non-technical, must be addressed to assess the general requirements of the proposed treatment system. These factors will ultimately affect the proper selection of a treatment process. Some of the issues that must be addressed before identifying and selecting the best treatment technologies are discussed below.

Influent Waste Stream Characteristics

The quantity, and the physical and chemical nature of the influent wastewater or groundwater must be evaluated. In many groundwater remediation projects, complex site hydrogeology can limit the engineer's ability to define the exact influent flow rates. This would suggest the need for designing flexibility into the system to accommodate a range of anticipated flows, or to facilitate modifications needed for changes in throughput during future operating years.

The presence of other organic and inorganic compounds could affect treatability of the influent when some technologies are considered. pH, total suspended solids (TSS), and temperature are some of the factors that could affect performance of the treatment system, or could increase capital or operations and maintenance (O&M) costs due to the need for pretreatment and byproduct or waste handling.

Facility Operating Life

Design life, or the duration which the facility is expected to operate, must be considered in the selection process. Generally, a wastewater treatment plant would be designed for a 20+ year operating life. However, the client may be projecting shorter term operation of the wastewater treatment facility, or the remedial plan for a groundwater cleanup installation may indicate a shorter cleanup time. The projected operating life could affect the selection of the treatment technology. The operating pattern throughout the life of the installation should also be considered. Will there be an increase or decrease in contaminant loading, flow or other water quality parameters over the life of the project? Significant changes in these parameters over the life of the project would need to be addressed in the technology selection phase to accommodate future facility expansion or a reduction in treatment capacity.

Does the system need to operate on a continuous, 24-hour per day basis, or will the plant be operated as a batch plant? Some technologies are difficult or time-consuming to start-up and shut-down, and operate most effectively at continuous, steady conditions. These would not be suitable for batch or single-shift operation.

Facility Operations

The client's ability and interest in operating, monitoring and maintaining the system during the life of the project should be addressed. What is the level of sophistication of the available

operators? In some instances, such as at a remote location, the unavailability of trained operators would require the use of a more sophisticated, automated system. Selection and installation of a low maintenance treatment system may be warranted in this case.

Regulatory Environment

There are often project-specific regulatory restrictions applied which can significantly affect the outcome of the technology selection. There may be an accelerated schedule imposed by the regulatory bodies that necessitates the selection of readily available, proven technologies that do not require lengthy pilot testing, or an extended detailed design and construction period.

Severe restrictions on disposal of water treatment system sludge or byproducts may necessitate the selection of treatment methods which generate a minimum quantity of waste products. Waste product disposal options must be evaluated early in the selection process, so that this can be taken into consideration.

Several permits which may be needed for application of certain treatment technologies such as air permits, sewer permits, discharge to surface waters, etc. could cause schedule delays and increase overall project costs. All of the necessary permits and procurement procedures should be identified for each potentially feasible technology.

Process Monitoring Requirements

Monitoring requirements for system performance monitoring and regulatory compliance will vary among the selected treatment options. Depending on the nature of the constituents in the influent water, the reliability of various technologies, and the "fail-safe" mechanisms designed into the treatment system, monitoring requirements can vary widely. Monitoring and analytical costs can be a significant cost component of ongoing system operations. The requirements should be assessed and considered during the technology screening and selection process.

Treatment Parameters

Treatment criteria must be established early in the technology screening and selection process. They should, if possible, be finalized with all appropriate regulatory and permitting bodies. Effluent criteria can vary significantly, depending on the point of discharge and applicable regulations governing the treatment plant operations. This will ultimately determine the

technical feasibility of each treatment process evaluated in the technology screening and selection process.

Site Specific Conditions

Utilities and site access, such as power, potable water and discharge piping to the sewer or waterway, roads, etc. may not be available at remote locations or may not be adequate for the project requirements. The cost of supplying such utilities and off-site improvements, etc. equal or exceed the cost of the treatment system. These should be assessed and included in any comparative cost analysis of potentially feasible technologies.

Site logistics and available plot space for installation of the treatment facility should be established, since application of some treatment technologies would require more area for the facility installation than others. Access for vehicles, heavy construction and maintenance equipment should be considered.

All of the above-noted components of the project definition should be carefully considered and should be considered in the final treatment process selection. Each factor will be weighted differently, and the relative importance of these factors will be unique. For each project, therefore, there can be no "typical" installations, or standard treatment costs associated with AOP or any other comparable technology.

APPLICABILITY OF AOP VERSUS STANDARD WATER TREATMENT TECHNOLOGIES

Advanced oxidation is frequently compared to carbon absorption, air stripping, and biologically activated sludge for wastewater or groundwater treatment. Depending on the nature of the contaminant and other specific requirements, there are numerous other technologies which may be applicable such as ozonation, use of other oxidants, wet-air oxidation, solvent extraction, photolysis, biologically activated carbon-packed columns, and other less commonly applied technologies. The applicability of these technologies compared to AOP will be addressed in this discussion.

Advanced Oxidation Processes (AOP)

Advanced oxidation processes (AOP) are a family of related reaction processes that have been used for the oxidation of organic compounds. All of these processes involve the generation of the highly reactive hydroxyl radical (OH.) as an intermediate product, and its subsequent

reaction with the targeted organic compounds. The most common commercially applied processes involve the use of various combinations of ultraviolet light (UV), ozone, and hydrogen peroxide. Selection of the most appropriate AOP process for a specific application depends on many variables. The overall effectiveness of AOP is quite specific to the organic constituents in the influent, water conditions, and the specific AOP process applied.

The most successful applications of this technology have been for treatment of contaminated groundwater and wastewater containing low-level concentrations (typically no higher than 50 to 100 mg/l) of chlorinated solvents, aliphatic aromatic hydrocarbons such as benzene, chlorinated phenolic compounds, water-soluble pesticides and metal/cyanide complexes.

Different organic constituents may be more treatable by one particular AOP process than another. Water chemistry can also affect treatability. Bicarbonate ion can act as a reaction inhibitor by "trapping" hydroxyl radicals. Inorganic compounds such as ferrous and manganous ions, sulphite, nitrite, and ammonium ions present in the influent may be preferentially oxidized and subsequently generate solids in the effluent stream. The presence of other organic compounds can slow the reaction if they are preferentially oxidized over the target organic constituents.

One of the major advantages of AOP over many other treatment technologies is its ability to not just remove, but destroy organic contaminants in the waste stream. It should be established during treatability testing that no undesirable reaction products are formed during the oxidation process.

The operating cost of most AOP systems is sensitive to the local cost of electricity, since most commercially available systems use large amount of power for UV light and/or ozone generation. Capital costs are highly sensitive to treatability or the targeted organic constituents as established during bench-scale testing. The destruction characteristics usually follow a pseudo first-order destruction curve and, therefore, residence time is a function of the desired destruction efficiencies. It is reasonable to expect up to about two decades of destruction, i.e., 99% destruction can be reasonably expected with a full-scale AOP treatment system.

Air Stripping

Air stripping involves the separation of volatile organic compounds from the aqueous waste stream into the vapour phase. Packed columns are commonly used to accomplish mass transfer. Air stripping is most commonly used for removal of halogenated organic solvents

and gasoline. Air stripping at ambient temperatures would not be effective for removal of low volatility compounds such as pesticides, many alcohols, pentachlorophenol, etc. Air stripping is applicable within the same range of contaminant concentrations as AOP, i.e., up to about 100 parts per million. Two decades of removal, i.e., 99% removal, can reasonably be expected on an ongoing basis. Adverse water chemistry, such as high total dissolved solids, high carbonate or high ferrous ion concentration can promote fouling and affect the effectiveness and maintenance costs of an air stripper. Fouling of the packing media with bacteria or inorganic compounds dissolved in the influent can necessitate routine cleaning or replacement of the column packing material. Air stripping is a process of mass transfer, i.e., transfer of contaminants from one media to the other. Unlike AOP, this is not a method of organics destruction.

Air stripping, when applicable, can be one of the most economical remedial technologies. However, vapour-phase contaminant recovery is frequently necessary, and pretreatment of the waste stream, if necessary, can affect the overall economics. The operations and maintenance costs are not highly sensitive to either removal efficiencies or flow rate, but rather the number of reactors used to obtain the treatment objectives.

Biological Activated Sludge

Biological degradation of organic contaminants can be effective at the parts per million levels of organics contamination. It is most suitable for destruction of contaminants from the hundreds or thousands of parts per million down to the parts per million range. Most biological systems usually do not consistently destroy contaminants below this level, and further organics removal, or "polishing", may be required to meet effluent criteria. There are many types of aerobic biological systems that fall into two major categories: suspended growth reactors (tanks, lagoons), or fixed-film reactors. The most common type, suspended growth reactors, will be discussed here.

Use of biological systems is contingent on the biodegradability of the target organics. Many man-made compounds such as chlorinated solvents do not readily biodegrade. At this stage of the technology, PCB's and dioxin are not effectively destroyed by biological treatment methods. Thorough bench-scale and pilot-scale is necessary prior to implementing most biological treatment systems to demonstrate the effectiveness of biodegradation on the influent waste stream.

There are several disadvantages to using biological treatment methods that should be noted. Although biological systems can be effective, economical and reliable, they require more sophisticated operations personnel to maintain a treatment facility. Improper operation, such as exposing the system to unexpectedly high levels of toxic constituents in the influent, can damage or kill the bacterial mass. Re-starting or acclimating the growth culture can require two to six weeks downtime. Depending on the flow rates and desired removal efficiencies, activated sludge systems can require more plot area than other comparable treatment methods.

Carbon Adsorption

Granular activated carbon (GAC) adsorption is commonly used for many wastewater, drinking water and contaminated groundwater applications. GAC is a well-demonstrated technology and is technically effective for many, although not all, organic constituents. However, GAC is only a means of transferring contaminants from the water phase to the carbon surface, and therefore can generate large quantities of spent carbon as a waste product. Water pretreatment for removal of suspended solids may be necessary to improve carbon adsorption. Operation of a GAC system usually requires very little operator involvement. Carbon is effective at removing organic compounds from water down to nearly non-detectable levels. For this reason, and because of its reliability, carbon is commonly used to "polish," or remove trace levels of contaminants downstream other treatment processes such as AOP or activated sludge systems.

The major drawback of GAC is the cost of carbon and its potential for generating a large solid waste stream. Carbon consumption is directly proportional to the mass loading, i.e., quantity adsorbed. Therefore, economics may not justify the use of granular carbon for higher contaminant levels, above the tens of parts per million range of adsorbable contaminants.

Other Treatment Methods

There are other technologies that may, in specific circumstances, be evaluated against AOP. Use of other oxidants such as ozone or hydrogen peroxide, chlorine dioxide, sodium hypochlorite, or potassium permanganate. Some of these may not have sufficient oxidative potential, or may produce undesirable by-products or oxidation products. However, if effective, implementation costs of using some of these oxidants could be highly favourable when compared against AOP.

New, innovative technologies such as wet air oxidation for higher influent contaminant levels, solvent extraction, and biologically reactivated packed carbon columns are among the available choices. Their effectiveness and economics will again depend on many project-specific factors.

CASE HISTORIES

CH2M Hill has been involved with approximately ten treatment technology screening and evaluation projects in which bench-scale treatability testing was conducted. One 70 GPM full-scale installation has been installed at a Tacoma, Washington RCRA Corrective Action Facility, and a second 500 IGPM full-scale system is in the final fabrication stages for installation in Elmira, Ontario. Extensive bench-scale treatability testing was conducted in our Redding, California laboratory under EPA contract comparing the kinetics of hydrogen peroxide/ozone oxidation on various chlorinated solvents. Additionally, CH2M Hill has implemented bench-scale testing and pilot-scale demonstrations at several industrial facilities across the country. The following discussion will focus on the full-scale installation at a RCRA Corrective Action Site in Tacoma, Washington.

Technology screening and treatability studies were conducted on contaminated groundwater for a RCRA corrective action at a pentachlorophenol manufacturing facility in Tacoma, Washington. Samples of contaminated groundwater underlying the site contained between 200 ppb and 5 ppm pentachlorophenol. Other miscellaneous contaminants, such as chlorinated solvents and petroleum hydrocarbons, were present in parts per billion ranges in several areas of the 52 acre site. One major concern of the groundwater sampled was its brackishness and high concentration of iron. Iron concentrations usually averaged 40 to 70 parts per million and were presumed to be ferrous ion. The clear, yellowish, groundwater quickly became turbid once bailed from the wells and exposed to the atmosphere.

Operating requirements were established during the technology screening and selection process. Discussions were opened with the local public wastewater treatment facility to procure an industrial pretreatment permit for treated effluent. A RCRA F021 waste designation was assigned to all recovered groundwater. This meant that all groundwater and wastes generated from its treatment were subject to RCRA land ban restrictions. Disposal of any treatment plant waste products, with the exception of the effluent discharge to the sewer would be costly, if at all possible. It was established early in the technology selection phase that only technologies which did not generate substantial amounts of sludge or other waste products would be considered.

The initial screening studies identified several technologies that were technically and economically feasible. Biological degradation (activated sludge), carbon adsorption and various methods of chemical oxidation were selected as potential treatment technologies. Solids disposal issues quickly eliminated both carbon adsorption and biological treatment as practical technologies for application at the site. Chemical oxidation by advanced oxidation processes was retained as a potentially applicable technology for groundwater treatment.

Three vendors of AOP technology were selected to conduct AOP treatability testing. Additional bench-scale testing of activated carbon was undertaken to confirm its applicability as a potential polishing step in the process. In addition to treatability testing, field visits were conducted at actual operating AOP installations to evaluate full-scale systems in operation and to discuss system performance with operations personnel. Comparative economical and technical evaluations were conducted before final selection of a UV/hydrogen peroxide AOP system. A 70 GPM system was leased as a "demonstration-phase" installation. If the demonstration-phase succeeded, the system would be placed permanently in a new operations building and placed in continuous service as a full-scale system.

Treatability testing had been successfully conducted on groundwater without pretreatment of the iron present in the groundwater. Although it was understood that iron removal might be necessary for the full-term, the demonstration-phase installation was installed without a pretreatment system. It was anticipated that the turbidity and hydrogen peroxide consumption attributed to iron oxidation could be incorporated into the sizing of the treatment system, and that acceptable reduction efficiencies could be achieved without generation of a solid waste stream.

The demonstration system was installed during construction of the numerous corrective action facilities around the plant. Many sources of contaminated construction water and surface runoff were available for the initial start-up. Successful reduction efficiencies of greater than 99% were achieved, although the water was at times quite turbid. It was suspected that high turbidity would affect UV light transmission and reduce destruction efficiencies. Start-up with groundwater was complicated by the presence of excessive iron in the water, up to 200 parts per million in some wells. It was anticipated that the excessive iron levels would subside once the wells were placed in continuous service; however, they have held relatively constant. The iron caused extreme fouling and coating of the UV quartz tubes; it required excessive tube cleaning.

Start-up testing was conducted on the system with pretreated (iron removed) groundwater and untreated groundwater. Results demonstrated that iron was significantly impeding system performance. Concurrently with receiving the results of the performance test, the negotiations for the discharge permit full-scale treatment system were discontinued and application for an NPDES permit for direct discharge to the local waterway was undertaken. Effluent quality requirements will be much stricter under an NPDES permit. This will significantly increase the treatment requirements for organic and inorganic compounds, and necessitate the installation of a metals pretreatment system where iron and trace heavy metals must be removed. Pretreatment technology screening is currently underway while the system operates intermittently with an interim pretreatment discharge permit to the local sewer.

CONCLUSIONS

AOP can be a technically effective option for destruction organic constituents when correctly applied. AOP is a new technology, with very few actual operating field installations. Our understanding and knowledge of the technology is increasing as we obtain more and more operating experience.

SESSION 2

THEORY, CHEMISTRY AND KINETICS

CHEMICAL MODELS OF ADVANCED OXIDATION PROCESSES

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ABSTRACT:

Advanced oxidation processes (AOPs) have been defined as ambient temperature processes which involve the generation of highly reactive oxyradicals, especially the hydroxyl radical. These processes show promise for the destruction of hazardous organic substances in municipal and industrial wastes and in drinking water. Three types of AOPs are considered in this paper: base-catalyzed decomposition of ozone; ozone with hydrogen peroxide (Peroxone); and photolysis of hydrogen peroxide with ultraviolet radiation. Kinetic models for these processes are being developed based on known chemical and photochemical principles. The models take into account measured effects of radical scavengers such as bicarbonate; dose ratios of the oxidants or UV intensity; and pH. The models are used to discuss two cases: oxidation of tetrachloroethylene in a pure water matrix and oxidation of nitrobenzene at relatively high concentrations.

INTRODUCTION:

Advanced oxidation processes (AOP) have been defined (1) as ambient temperature processes that involve the generation of highly reactive radical intermediates, particularly the hydroxyl radical (OH). Conceived and extensively applied in essentially empirical fashion, AOPs have lately been the subject of more fundamental studies to establish their chemical mechanisms and to maximize their efficiencies through the application of good engineering principles (2-17).

The appeal of AOPs is the prospect of complete oxidation of organic contaminants through a "combustion" process that operates at or near ambient temperature and pressure. This has been realized for the treatment of ground water containing simple organic halides such as tri- and tetrachloroethylene (13,14) and 1,2-dibromo-3-chloropropane (17) which are essentially mineralized by AOPs. It is unlikely, however, that complete mineralization will be realized

in most cases, but AOPs are still likely to be useful pretreatment processes that are complementary to other processes. In particular, AOP will combine nicely with biological oxidation for the removal of compounds that are too refractory or too toxic for biological degradation to be a practical alternative (18).

The oxidative power of AOPs is due largely to the very highly reactive OH radical whose rate constants with many typical organic compounds have been documented in the basic chemical literature and well known to atmospheric and nuclear scientists. Rate constants for the reaction of several organic compounds with the OH radical are shown in Table 1 (19).¹

TABLE 1
RATE CONSTANTS FOR THE HYDROXYL RADICAL
(Buxton et al., 19)

Compound, M	$k_{M,OH} \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
Benzene	7.8
Toluene	3.0
1-Butanol	4.2
Vinyl Chloride	7.1
Trichloroethylene	4.0
Tetrachloroethylene	2.3
Pyridine	3.8
Chlorobenzene	4.5
Nitrobenzene	3.9
Hydroperoxide Ion, HO_2^-	7.5
Dichloromethane	0.058
Chloroform	- 0.005
Carbon Tetrachloride	NR
Bicarbonate Ion	0.0085
Carbonate Ion	0.39

¹ It is clear from Table 1 that hydroxyl radicals are not very reactive toward chlorinated methane compounds. The rate is proportional to the number of hydrogen atoms in the molecule. AOPs are, therefore, of marginal usefulness in the treatment of chloroform contaminated waters and of no use for the removal of carbon tetrachloride.

These constants refer to second-order chemical processes where the rate of primary oxidation of the compound M is given by the expression:



$$R_{M,OH} = -d[M]/dt = k_{M,OH} [M][OH]_{ss} \quad (1)$$

where $[OH]_{ss}$ is the steady-state concentration of OH radicals formed in the AOP. If $[OH]_{ss}$ is a constant, i.e. if the steady-state assumption holds, equation (1) predicts that a plot of $\ln[M]$ vs. time will be a straight line with slope equal to $k_{M,OH}[OH]_{ss}$ no matter how complicated the chain mechanism that forms OH. A number of experimental studies have shown this to be the case (15,16) (Figure 1). The slope of such plots is often referred to as the pseudo-first order decay constant for substrate M, $k_{o,M}$:

$$k_{o,M} = -d(\ln[M])/dt = k_{M,OH} [OH]_{ss} \quad (2)$$

and one can calculate the time (t_n) required for oxidation of M from its initial concentration $[M_0]$ to $[M_0/e^n]$, where e is the base of natural logarithms:

$t_n = n/k_{o,M}$	n	% decomposition M
	1	63
	2	86
	3	95

As we shall see, however, advanced oxidation processes are not always kinetically first order in substrate M.

CHEMICAL MODELS OF AOPs:

The purpose of chemical kinetics modeling is to provide a comprehensive understanding of a process which details in mathematical form the effect of various independent variables on the rate constant $k_{o,M}$. Unfortunately, few environmental systems are sufficiently simple to allow us to model them explicitly, so empirical studies of AOPs must be done to determine the suitability of an AOP for treatment of a given process stream. Nonetheless, chemical models are of value in process design and economic evaluation, and they are useful in that they often suggest experimentation to test the mechanism used to formulate the model.

This paper will not be an exhaustive treatment of AOP models. Rather, we shall briefly examine three case studies to illustrate some features of AOPs and the value of chemical modeling in designing experimental protocols for optimizing these processes.

Ozonation as an AOP.

Stachelin and Hoigné (20) were among the first to build chemical models for AOPs. Based on the chemical mechanism shown in Figure 2, they derived a formula for the steady state concentration of OH radicals in a system containing ozone and a generalized substance M which is undergoing oxidation. With the assumptions of their model, the steady state OH concentration is given by:

$$[\text{OH}]_{ss} = \frac{2k_i[\text{OH}^\cdot] + k_t[\text{M}]}{\sum_i k_{s,i}[\text{S}_i] + k_{s,M}[\text{M}]} [\text{O}_3] \quad (3)$$

where k_i and k_t refer to rate constants for the initiation of the reaction by hydroxyl ions and by M itself, respectively, and $k_{s,i}$ and $k_{s,M}$ refer to the scavenging of OH radicals by substances S_i and M, respectively. Scavenging is a term used for reactions of substances with OH radicals that do not yield species that propagate the chain reaction. In many natural water systems the principal scavengers are carbonate and bicarbonate; thus, equation (3) may be modified to explicitly take into account these species. Equation (3) then becomes (4):

$$[\text{OH}]_{ss} = \frac{2k_i[\text{OH}^\cdot][\text{O}_3] + k_t[\text{M}][\text{O}_3]}{k_{s,M}[\text{M}] + \sum_i k_{s,i}[\text{S}_i] + (k_{\text{HCO}_3, \text{OH}} + k_{\text{CO}_3, \text{OH}} 10^{\text{pH} - \text{pK}'}) [\text{HCO}_3^-]} \quad (4)$$

where $k_{\text{HCO}_3, \text{OH}}$ and $k_{\text{CO}_3, \text{OH}}$ are rates of scavenging of OH by bicarbonate and carbonate respectively and pK' is for the carbonate-bicarbonate equilibrium.

Equation (4) may be substituted into equation (2) to obtain an expression for $k_{o,M}$ but the equation will contain a term for the ozone concentration $[\text{O}_3]$. In the batch systems used by Stachelin and Hoigné the ozone was added only at the beginning of a reaction. Under these conditions, the rate of disappearance of ozone is given by equation (5):

$$-(d(\ln[O_2])/dt) = k_1[OH^\cdot] + \frac{(2k_1[OH^\cdot] + \sum_i (k_{t,i}[M_i])) \left(1 + \frac{\sum_i (k_{p,i}[M])}{\sum_i (k_{s,i}[M])} \right)}{\sum_i (k_{s,i}[M])} \quad (5)$$

where the subscript i refers to different species that may initiate a chain by reaction with ozone, and propagate or terminate a chain by reaction with OH radicals. Staehelin and Hoigné followed the concentration of ozone in their batch system and showed that equation (5) rationalized the data well. Their emphasis was not on destruction of substrates, which is our focus.

In practice, ozone is usually added constantly so a function describing $[O_2]$ with time is needed. In a semi-batch reactor, the rate of transfer of ozone is assumed to be:

$$(d[O_2]/dt)_i = k_L a (P/H - [O_2]) \quad (6)$$

where P is the partial pressure of ozone in the gas phase entering the reactor and H is the Henry's Law constant for ozone-water:

$0.082 \text{ m}^3\text{-mole}^{-1}\text{-atm}$. The result is equation (7):

$$-(d(\ln O_2)/dt) = k_1[OH^\cdot] - (1/[O_2]) \{ k_L a (P/H - [O_2]) + \frac{(2k_1[OH^\cdot] + \sum_i (k_{t,i}[M_i])) \left(1 + \frac{\sum_i (k_{p,i}[M])}{\sum_i (k_{s,i}[M])} \right)}{\sum_i (k_{s,i}[M])} \} \quad (7)$$

This equation and equations (2) and (4) may be combined to model several AOP scenarios involving ozone.

Ozone-Hydrogen Peroxide (PEROXONE).

This system has been described in detail in recent papers (15,16) and the derivation of the model will not be repeated in detail here, except to note that previous derivations have not taken into account the formation of promoters such as HO_2 during the reaction. When no such promoters are formed and inorganic carbon species are the principal OH scavengers, the

expression for the pseudo-first order rate constant $k_{o,M}$ for a micropollutant M is given by equation 8, provided the dose rate of hydrogen peroxide exceeds the stoichiometric ratio required for complete consumption of ozone ($H_2O_2: O_3 > 0.5$, mole:mole):

$$k_{o,M} = \frac{k_{M,OH} k_L a P/H}{k_{M,OH}[M] + (k_7 10^{pH-pK} + k_8)[H_2O_2] + (k_{10} + k_{11} 10^{pH-pK})[HCO_3^-]} \quad (8)$$

In equation (8), the term $(k_7 10^{pH-pK} + k_8)[H_2O_2]$ represents reaction of OH with hydrogen peroxide and its conjugate base, and $(k_{10} + k_{11} 10^{pH-pK})[HCO_3^-]$ is for reaction of OH with bicarbonate and carbonate respectively.

Glaze and Kang have shown that this equation and observed $k_{o,M}$ values can be used to measure values of $k_{M,OH}$ which are in agreement with values in the literature, and that the effect of inorganic carbon species is correctly predicted by equation (8) (15,16).

An interesting feature of equation 8 is that it predicts that the peroxone process will become zero order in M when M is the principal OH scavenger. As we shall see, this behavior is observed for oxidation of concentrated solutions of nitrobenzene.

UV Photolysis of Hydrogen Peroxide.

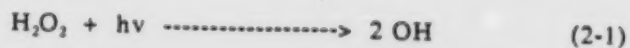
This process has been examined in detail by Guittonneau et al (21) and more recently by Glaze and Lay (17). The principal reactions of the system are shown in Table 2. For the case of one substrate M which is both a radical scavenger and UV absorber, the expressions for the steady state concentration of OH radicals is as follows:

$$[OH]_{ss} = \frac{2 \phi I_o (1 - \exp(-a_{H_2O_2} b [H_2O_2]))}{k_2 [H_2O_2] + k_3 [HO_2^-] + (k_{HCO_3, OH} + k_{CO_3, OH} 10^{pH-pK'}) [HCO_3^-]} \quad (9)$$

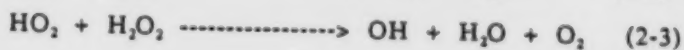
where I_o is the effective incident radiation power. If there are no other significant absorbers present, I_o is essentially the true incident power.

TABLE 2. PRINCIPAL REACTIONS IN THE H_2O_2 /UV SYSTEM.

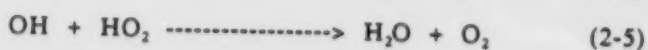
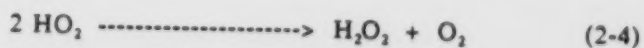
Initial Reaction



Haber-Weiss Cycle



Termination



If on the other hand, there are strong absorbers present other than peroxide, the net effect will be as if I_0 were decreased, i. e. there is less incident power available to the peroxide. Hence, the amount of radiation converted into OH radicals will be proportionately less if such absorbers are present. In some cases radiation absorbed by other absorbers can be beneficial for treatment if: (a) the absorber is M and direct photolysis results; (b) the absorber causes M to decompose by a photosensitization process. The overall rate of decomposition of M will be:

$$-d[M]/dt = k_p + k_{ps}[PS] + k_{M,OH}[OH]_M[M] \quad (10)$$

where k_p is the rate constant of direct photolysis of M, k_{ps} is the rate constant for induced decomposition by the photosensitizer PS.

The solution of the equations for the photolysis of peroxide in relatively pure water containing a model substrate M have been discussed by Glaze and Lay (17).

CASE STUDIES OF AOPs:

In this section we will examine two case studies: (1) the oxidation of tetrachloroethylene in highly purified water and the effect of pH and inorganic scavengers thereon; and (2) the oxidation of nitrobenzene in relatively concentrated solutions.

Case A: Ground Water (Low concentration of PCE, high concentration of bicarbonate, pH variable, M does not initiate or propagate chain. Comparison of ozonation and Peroxone.

Ozonation. Under these conditions, equations (4) and (7) simplify to (11) and (12):

$$k_{o,M} = \frac{k_{M,OH} 2k_i[OH][O_3]}{(k_{HCO_3,OH} + k_{CO_3,OH} 10^{pH-pK})[HCO_3^-]} \quad (11)$$

$$-(d[O_3]/dt) = 3k_i[OH][O_3] - (k_{La}(P/H - [O_3])) \quad (12)$$

Equation (12) may be rearranged and integrated to yield equation (13).

$$[O_3] = A/B (1 - \exp(-Bt)) \quad (13)$$

where $A = k_{La}(P/H)$ and $B = (3k_i[OH] + k_{La})$. Since all of the terms in equations (11) and (13) are known, one can calculate projected rates of oxidation for a model substrate such as tetrachloroethylene, whose $k_{M,OH}$ value is $2.3 \times 10^9 M^{-1}s^{-1}$. The results are shown in Figure 3 for a typical semi-batch reactor at several pH values using water that is 4 mM in total inorganic carbon. In the Figure 4 percent conversion of PCE is shown as a function of time and it is seen that complete oxidation of PCE is not achieved after 1000 seconds (16.7 minutes) contact time. Note that maximum conversion is achieved at pH 9 where one has a balance of two forces: enhanced rate of decomposition of ozone to OH radicals, and minimization of bicarbonate-carbonate scavenging of OH. In Figure 5 this effect is apparent (note here that pseudo-first order rate constants are plotted, being taken from the slopes of the data in Figure 3 which are close to straight lines because the exponential term in equation reduces to a linear term at low values of the exponent).

Figure 5 also shows a comparison of the rates of PCE oxidation in the presence of 4 mM and 0.4 mM total inorganic carbon. Note that the value of $k_{o,M}$ is enhanced by a factor of about seven by the decrease in alkalinity at pH 9. This means that half-life decreases from about 20 minutes at 4 mM to about 3 minutes at 0.4 mM. At the ozone dose being used (0.23 mg/L-min), this means a saving of 3.9 mg/L ozone, or 84%. In other words, direct ozonation of a micropollutant such as PCE can be affected in a ground water but pH adjustment is an imperative and bicarbonate softening will be essential in high alkalinity waters.

Peroxonation. It is interesting to compare the results in Figure 5 with data and predictions for Peroxone oxidation of PCE (15,16). Figure 6 shows rates of Peroxone oxidation of PCE at several pH values and Figure 7 shows this and the data in Figure 5 plotted together. It is seen that peroxone oxidation rates are 1.3 to 92 times faster than with ozone alone.

Case B: Industrial Process Stream (High Concentration of organic pollutant (nitrobenzene), low concentration of other scavengers).

This very complex case will be illustrated with some recent data in which we have studied the oxidation of nitrobenzene with ozone, Peroxone and peroxide/UV.

Peroxonation and Ozonation. Figure 8 shows Peroxone data for two runs where the ozone and peroxide doses are the same and where the initial nitrobenzene is 50 and 100 ppm. At the higher concentration the plot of concentration vs. time appears to be linear, i.e. the reaction is zero order. At the lower concentration the plot has curvature, appearing to change order about half-way through the run.

Figure 9 shows the evolution of the concentration of peroxide during the run at $NB_0 = 50$ ppm. The Limiting Value line represents the feed rate of peroxide into the reactor, i.e. with no reaction. It is clear that at the beginning of the reaction little peroxide is utilized and after 120 minutes of reaction the peroxide residual is almost two-thirds of that of the limiting value.

Figure 10 shows plots of NB/NB_0 for an "ozone only" run and for Peroxone runs with peroxide doses of 0, 0.3, 0.5 and 1.0 times the ozone dose (w/w). It is clear that the rate of oxidation of nitrobenzene under these conditions is independent of the concentration of peroxide. Also, it is observed that no ozone residual is present in any of these runs (data not shown).

Figure 11 shows that bicarbonate has essentially no effect on the oxidation of nitrobenzene under these conditions. (Sodium hydroxide solution was added in the unbuffered case so that the pH would not decrease substantially during the reaction).

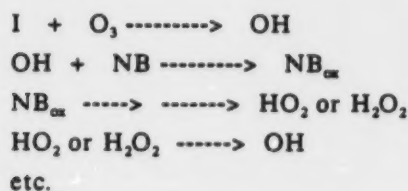
These observations are consistent with our current understanding of AOPs but a precise chemical model of the system is not yet available. It is possible, however, to rationalize the data in terms of current models and in so doing, to draw some interesting conclusions.

First, the zero order of the peroxone data at high concentrations of M and the lack of an effect of added bicarbonate is due to the predominance of the $k_{M,OH}[M]$ term in the denominator of equation (8). At moderate initial concentrations of M (Figure 8), the rate becomes of transitional order as the terms in the denominator become more comparable.

The fact that the "ozone only" run shows oxidation rate of nitrobenzene equal to the Peroxone runs, and that the Peroxone rates are independent of peroxide feed rate are surprising at first, but upon reflection make sense. It should be understood that the "direct" reaction of ozone with NB is quite slow. For example, at a concentration of NB of 1 mM and an ozone residual of 0.48 mg/L (never achieved in these runs), the rate of ozonation of NB is given by equation (14):

$$\begin{aligned}
 -d[NB]/dt &= k_{NB,O_3}[O_3][NB] \\
 &= (9 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1})(1.0 \times 10^{-5} \text{ M})(1 \times 10^{-3}) \\
 &= 9 \times 10^{-10} \text{ M s}^{-1} = 5.4 \times 10^{-8} \text{ M min}^{-1}
 \end{aligned}
 \tag{14}$$

Figure 10 shows that the rate of NB oxidation in the ozone only run is about 0.41 ppm per minute ($3.3 \times 10^{-6} \text{ M-min}^{-1}$). Clearly, direct ozonation of NB is not responsible for the disappearance of the material in the ozone only run. Apparently, some other substance is present which initiates the reaction producing OH radicals which then produce a chain reaction:



In the case of industrial wastewaters, it is highly probable that some substance will be present which will initiate the decomposition of ozone, producing OH radicals. If there are substances present that then react with the OH radicals to eventually produce chain propagating agents such as hydroperoxyl radicals or hydrogen peroxide, the chain reaction will continue to consume the substrate and ozone. In the case studied here, NB is probably not the initiator. More likely, impurities in the NB (said to 99% pure by the manufacturer), probably nitrophenols, are the probable initiators.

Photolysis of Hydrogen Peroxide. Figures 12 and 13 show the results of runs in which NB is initially at 50 ppm and the concentration of peroxide is varied from 0.05 to 12 mM (1.7 to 408 ppm). Four 25 watt low pressure mercury arc lamps were used with a total power at 254 nm of 0.48 watts/L. The results are informative only in that they show how the peroxide/UV process depends upon the absorption of photons by the peroxide. Since the extinction coefficients of NB and peroxide at 254 nm are 6150 and $18 \text{ M}^{-1}\text{cm}^{-1}$ respectively, at the concentrations used in these experiments NB is absorbing essentially all of the UV radiation. Thus, peroxide is hardly decomposing (Figure 14) and few OH radicals are generated. The decomposition rate of NB (Figure 12 and 13) is extremely slow (half-life of 106 min at 8 mM peroxide).

The conclusions from this case study are as follows:

- a. Highly concentrated wastewaters may be oxidized first by direct ozonation followed with polishing by a more powerful AOP.
- b. More concentrated wastewaters may not be subject to scavenger effects by inorganic carbon unless the latter is present at very high concentrations relative to the target substrate.
- c. As an AOP reaction proceeds to completion, the order of the reaction may shift from zero order in substrate to first order, scavenging effects will become more pronounced, and the overall efficiency of OH utilization will decrease.
- d. Photolysis of hydrogen peroxide is most effective as an AOP if the substrate does not dominate UV absorption or if so, it photolyses with high efficiency.

OH RADICAL UTILIZATION IN AN AOP:

In previous works (13-16), it has been shown that the Peroxone system is not very efficient for the oxidation of a micropollutant at low concentrations (ppb range), particularly if there are powerful scavengers present such as inorganic carbon. For oxidation of 100 ppb PCE in 4 mM total inorganic carbon at pH 7 (primarily bicarbonate), it can be shown that only about four percent of the OH radicals produced react with PCE. At higher concentrations the fraction increases; i.e. at 100 ppm PCE and 4 mM inorganic carbon, the percentage of OH radicals scavenged by PCE rises to 98%, that is provided the by-products of the initial OH attack do not themselves consume OH radicals. In the case of PCE, it is likely that the by-products do

not require further OH radicals; rather, they decompose by hydrolysis and reaction with dioxygen (Glaze, Kang and Shovlin, unpublished work). In the case of nitrobenzene, it is almost certain that the by-products react both with ozone and with OH radicals, so the reaction is less efficient. We estimate that overall utilization of OH radicals by substrate (initially at 50 ppm) is about 19%. But, as the reaction proceeds the radical process becomes less and less efficient.

In summary, Advanced Oxidation Processes are extremely complex reaction systems. However, they are amenable to chemical modeling in the simplest cases (ground water and highly pure water treatment), and even in the case of more complex systems models can reveal features of the processes that may be exploited.

ACKNOWLEDGEMENT:

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FIGURE 1

OXIDATION OF PCE WITH PEROXONE

Ozone Dose: 0.23 mg/L-min

Bicarbonate: 4 mM

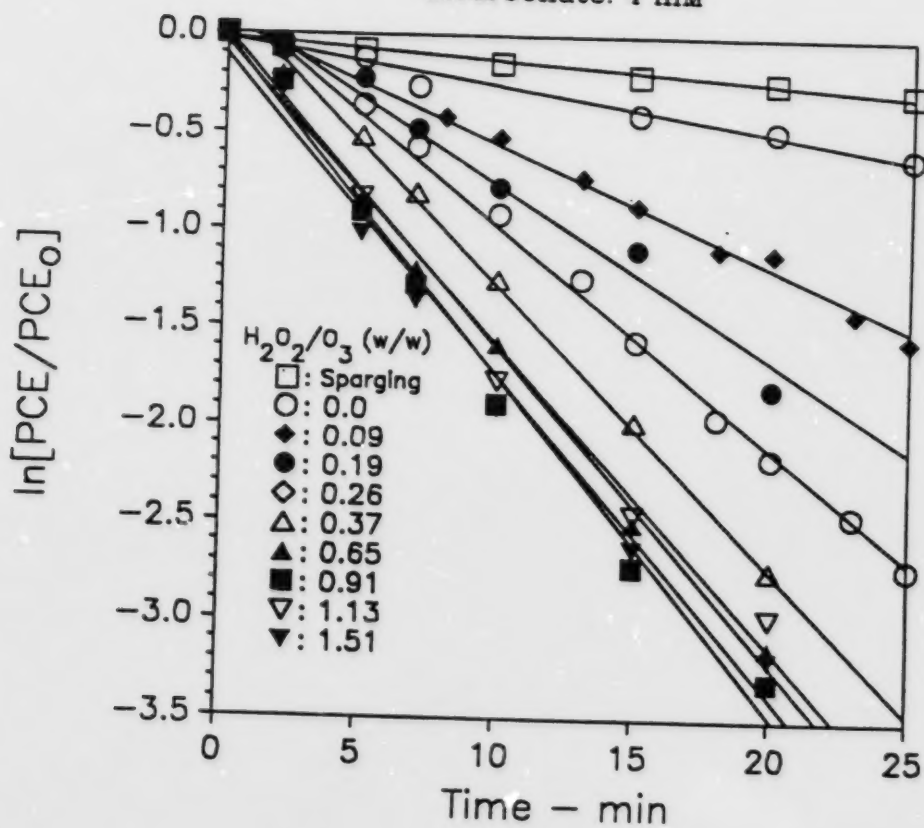


FIGURE 2

OZONE DECOMPOSITION SCHEME (Hoigne et al)

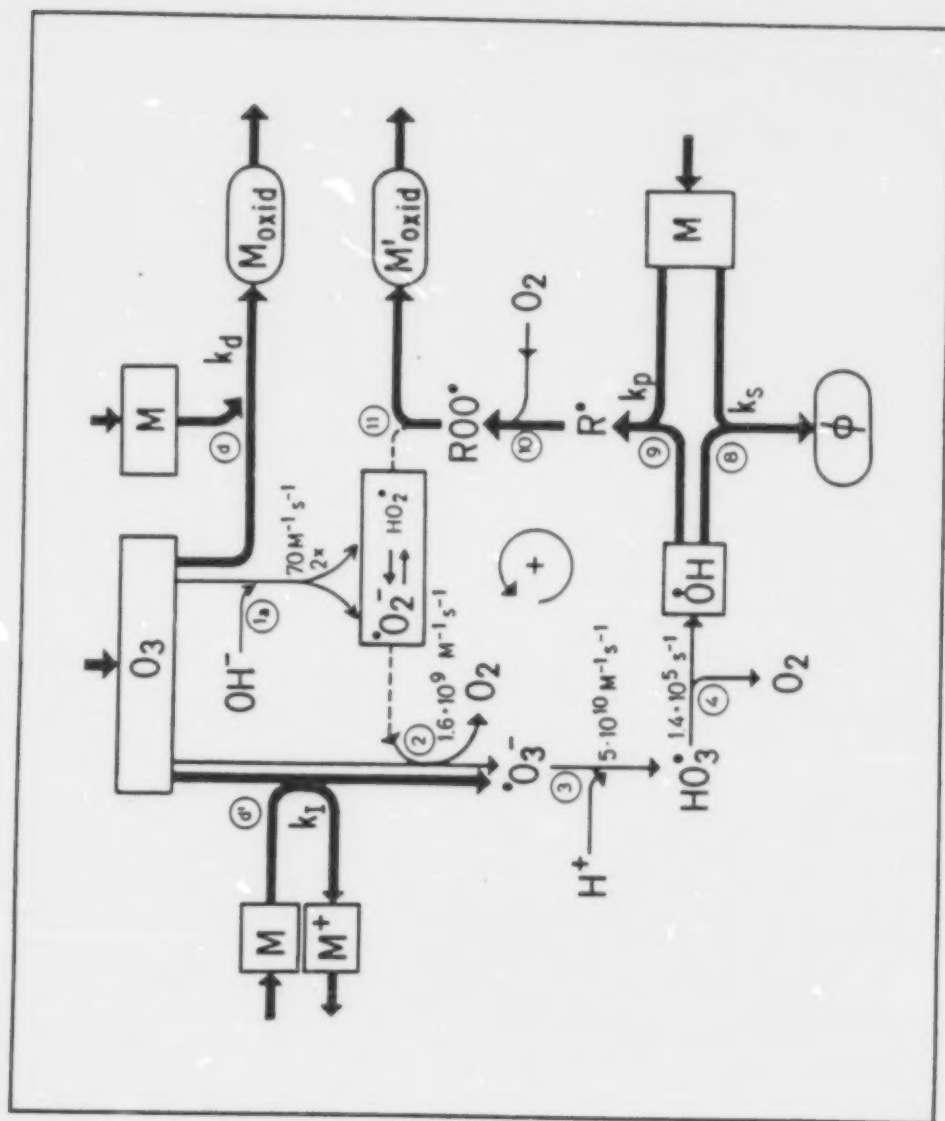


FIGURE 3

PREDICTION OF REMOVAL RATE OF PCE BY OZONE AOP

Ozone : 0.23 mg/L-min

C_T, CO_3 : 4 mM

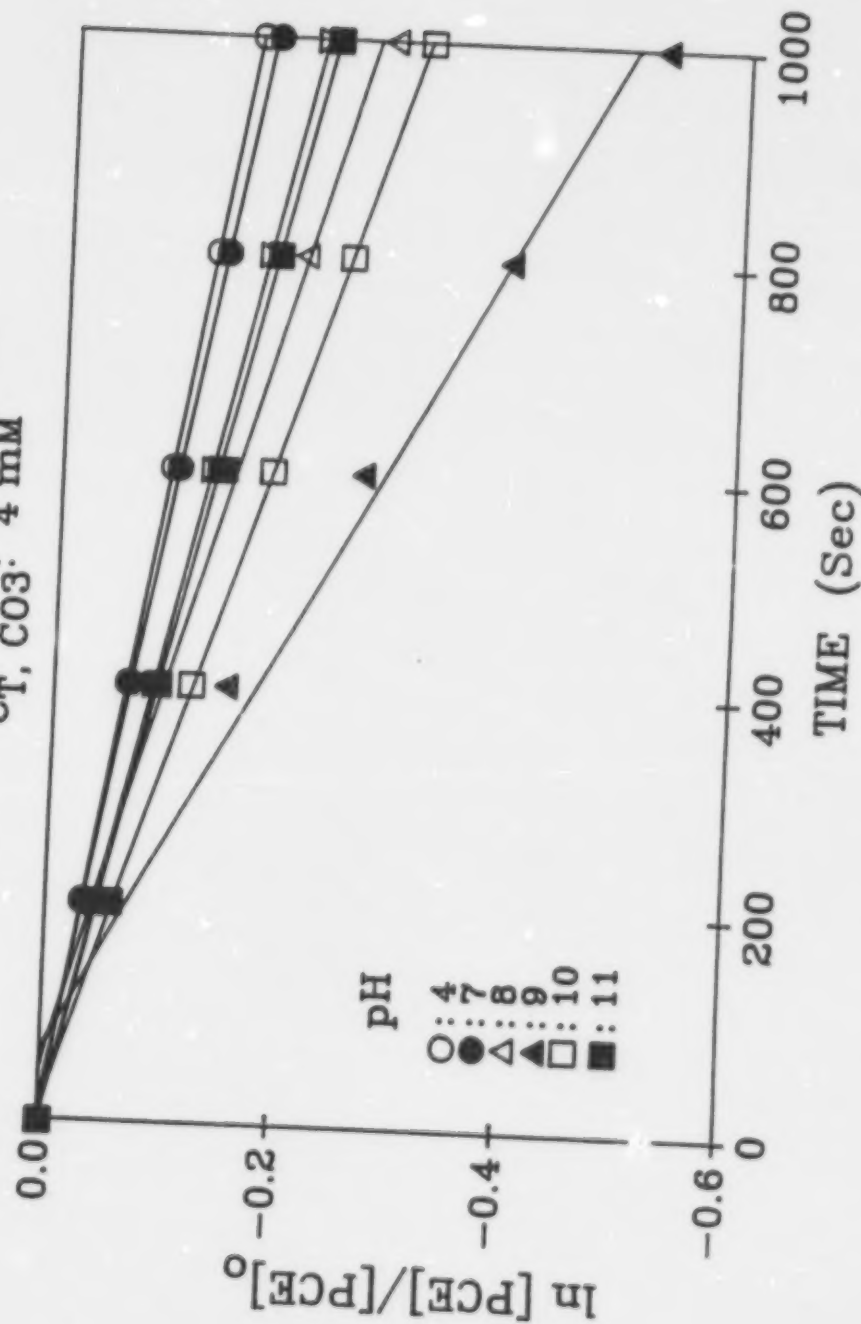


FIGURE 4
PREDICTION OF PCE REMOVAL BY OZONE AOP

Ozone: 0.23 mg/L-min

C_T, CO_3 : 4 mM

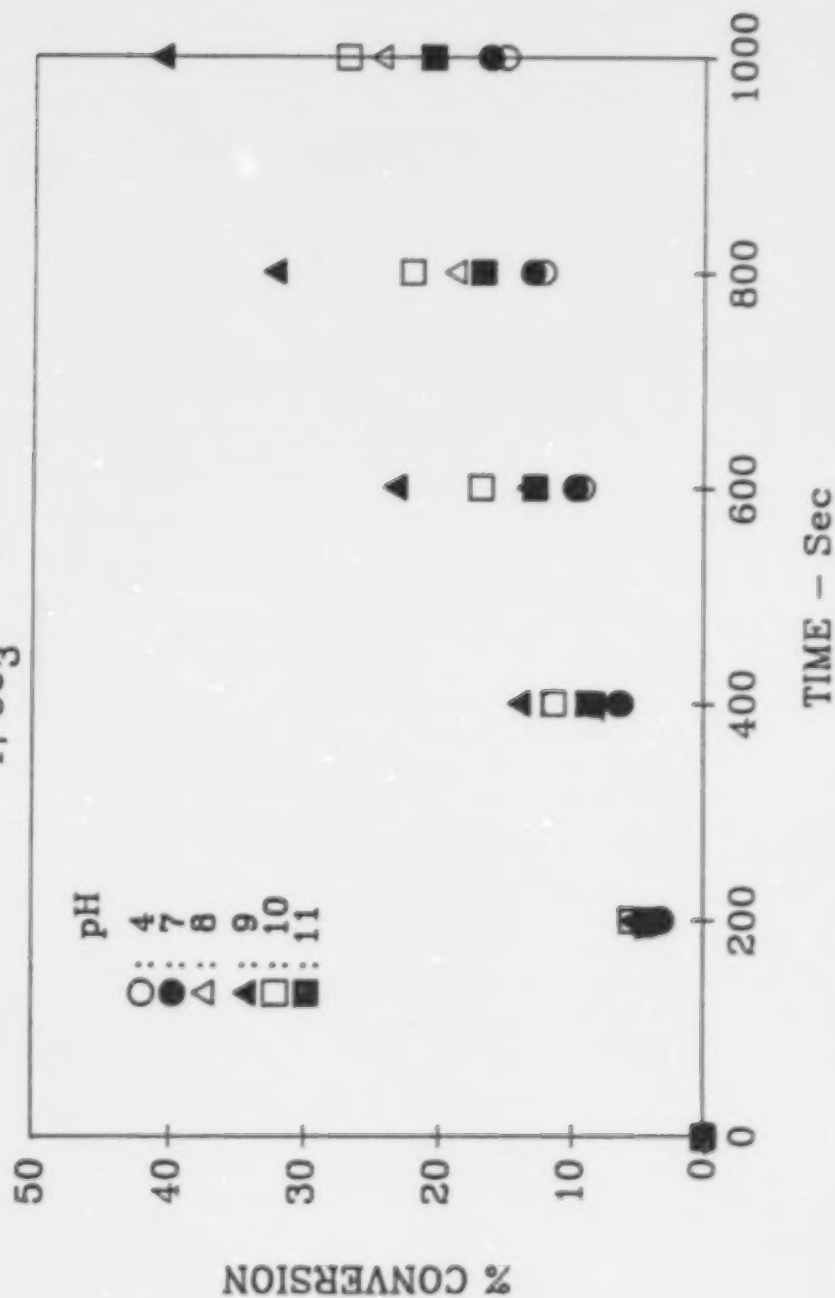


FIGURE 5

OXIDATION OF PCE WITH OZONE

Ozone Dose: 0.23 mg/L-min

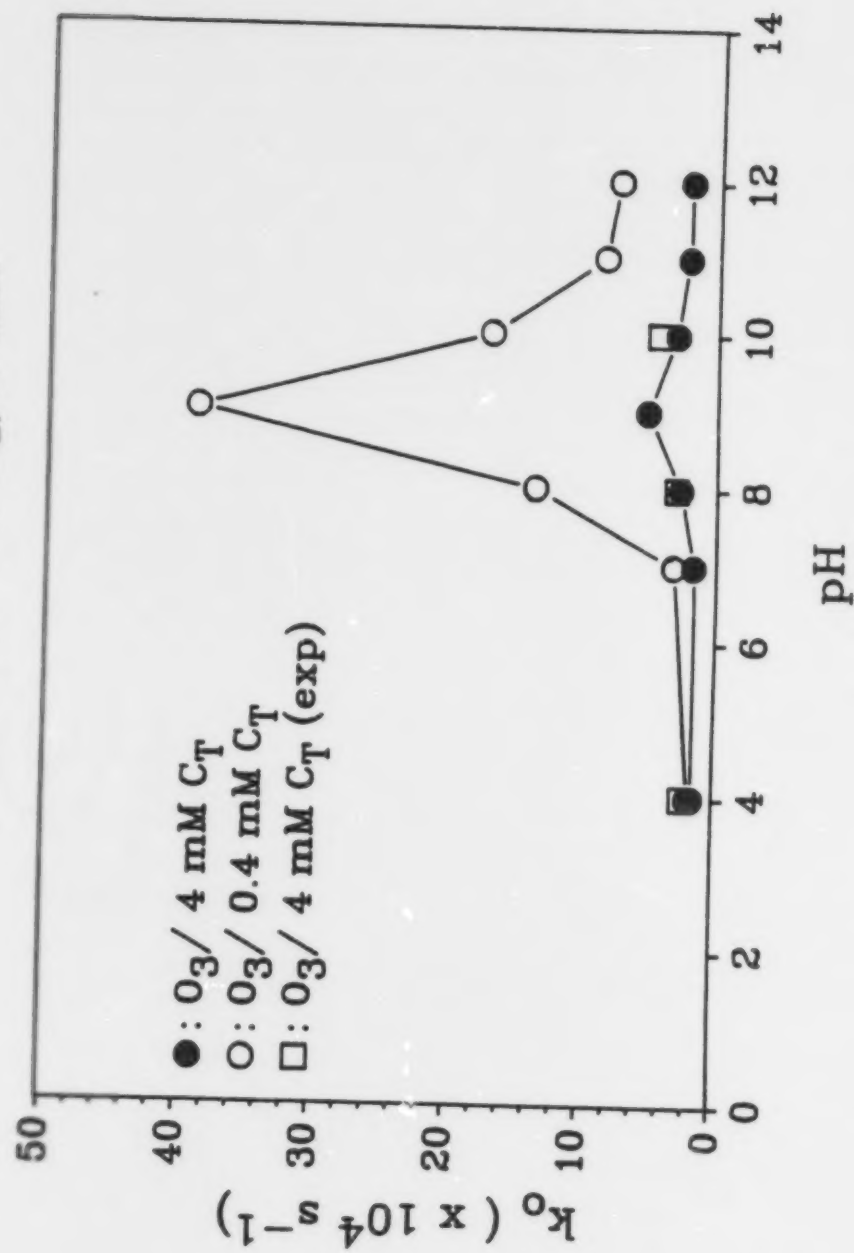


FIGURE 6
OXIDATION OF PCE WITH PEROXONE

Ozone Dose: 0.23 mg/L-min

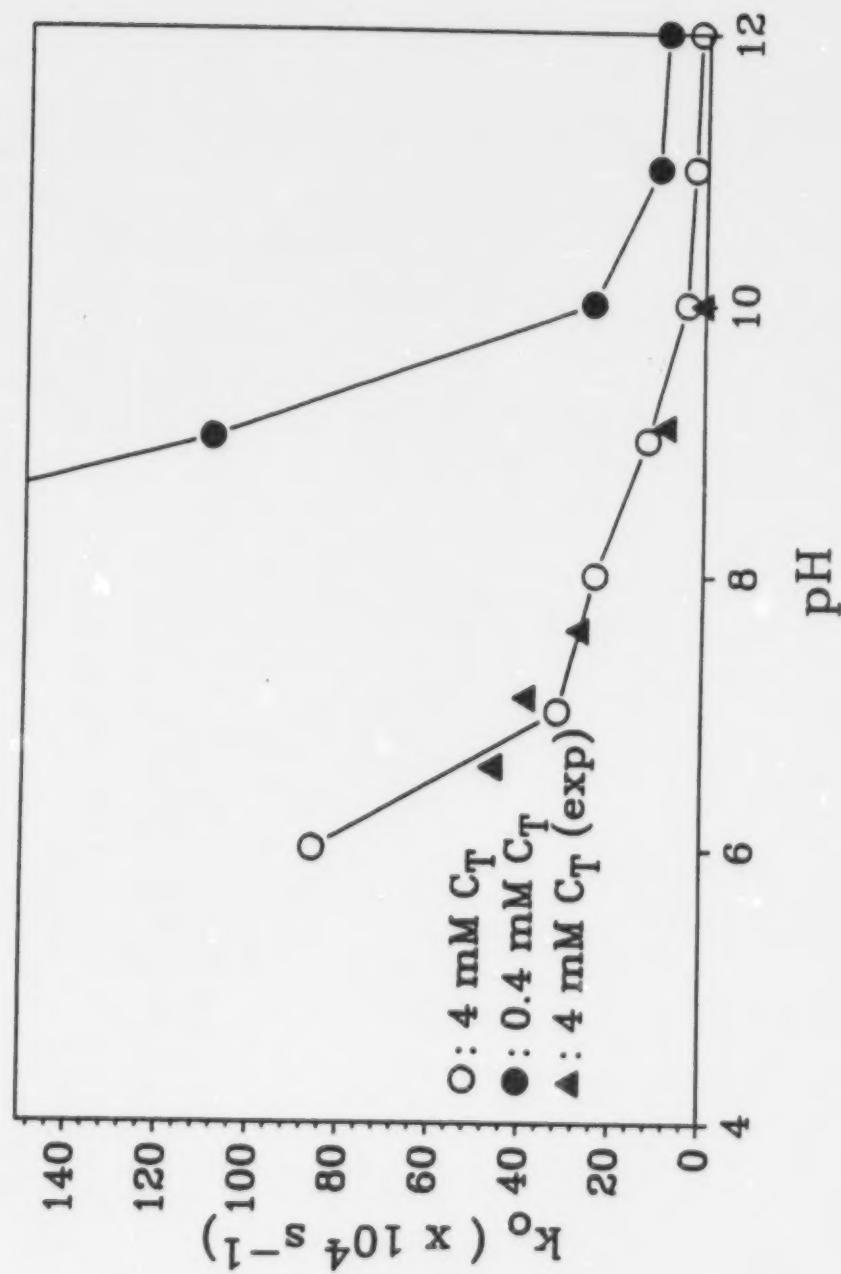


FIGURE 7

OXIDATION OF PCE WITH OZONE & PEROXIDE

Ozone Dose: 0.23 mg/L-min

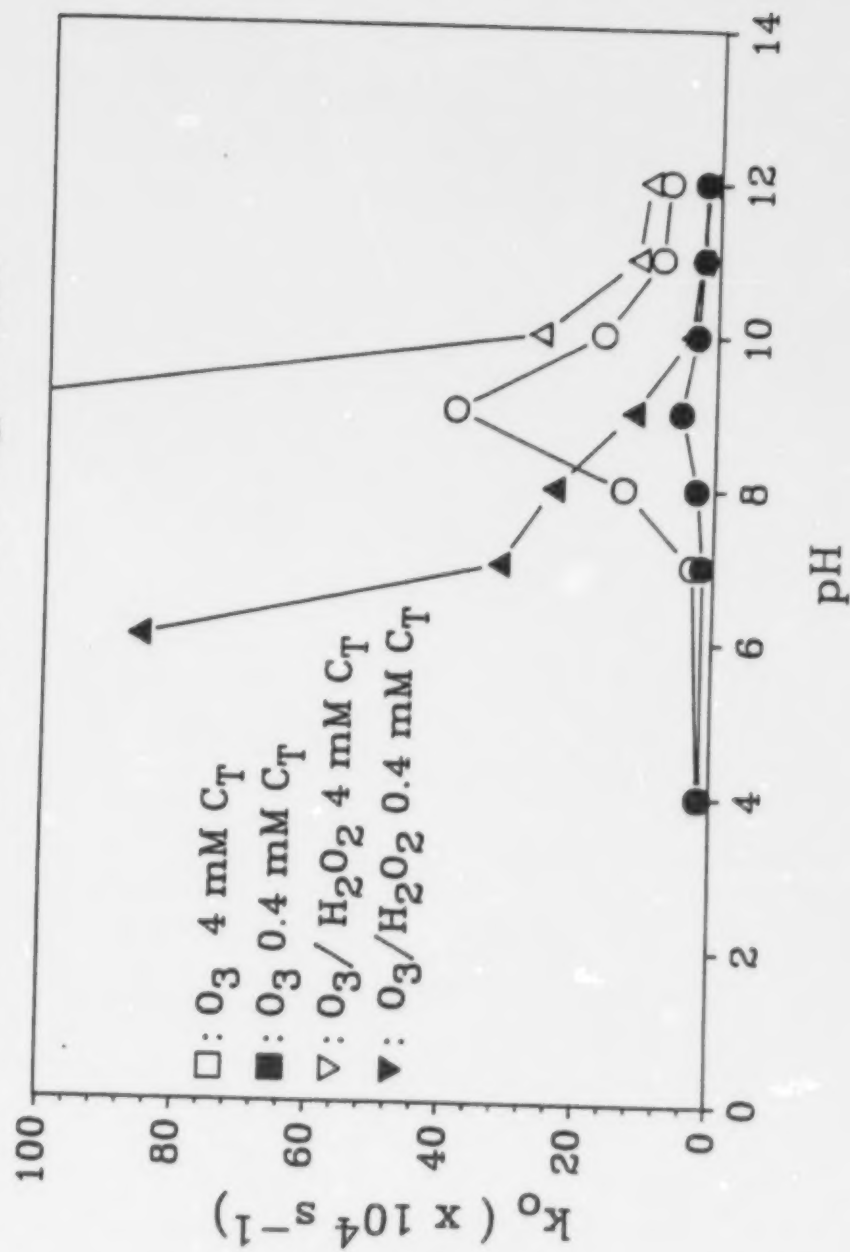


FIGURE 8

PEROXONE OXIDATION OF NITROBENZENE

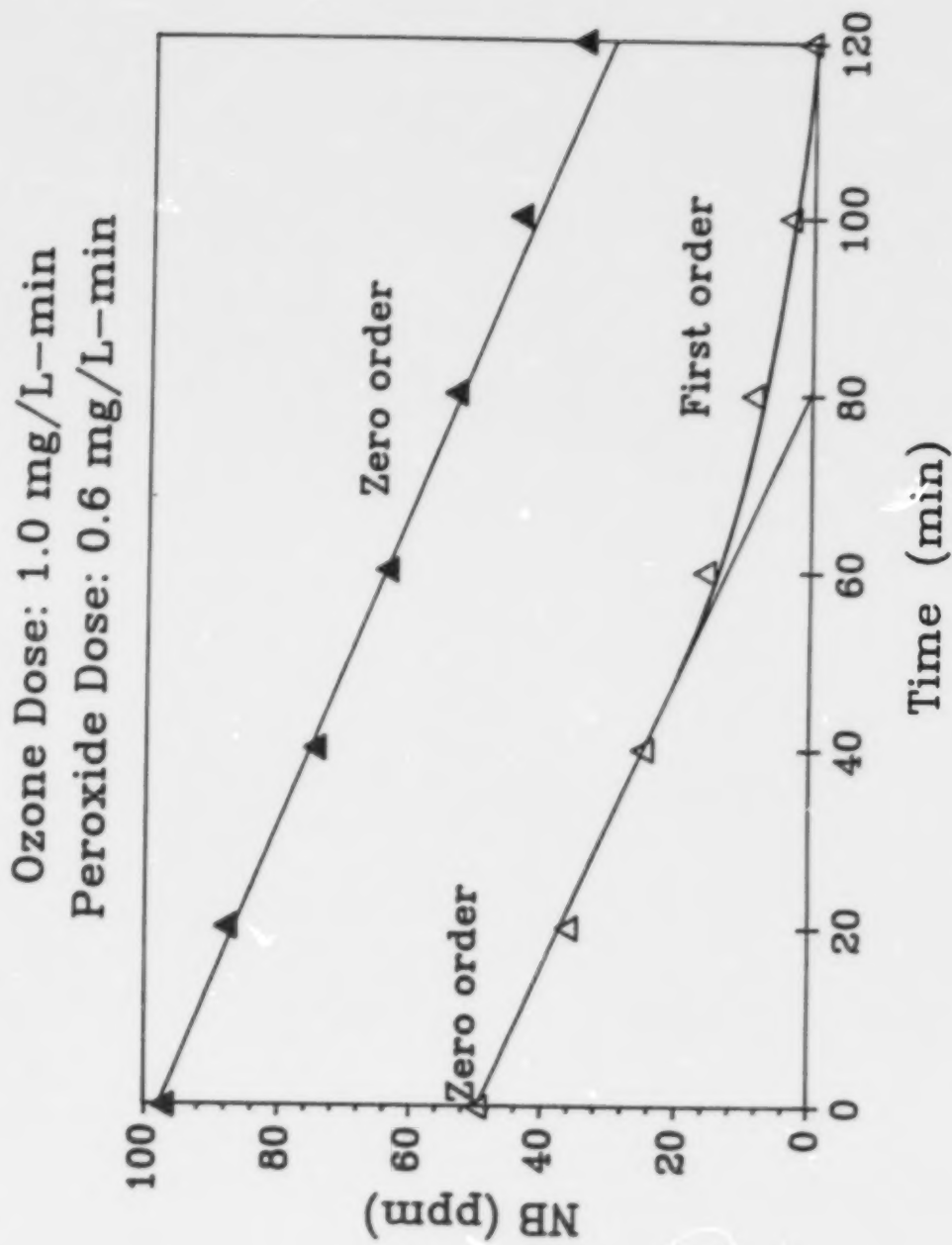


FIGURE 9

HYDROGEN PEROXIDE BUILD-UP PATTERN

Ozone Dose: 1.0 mg/L-min

Hydrogen Peroxide: 0.6 mg/L-min

$[NB]_0 = 50 \text{ mg/L}$

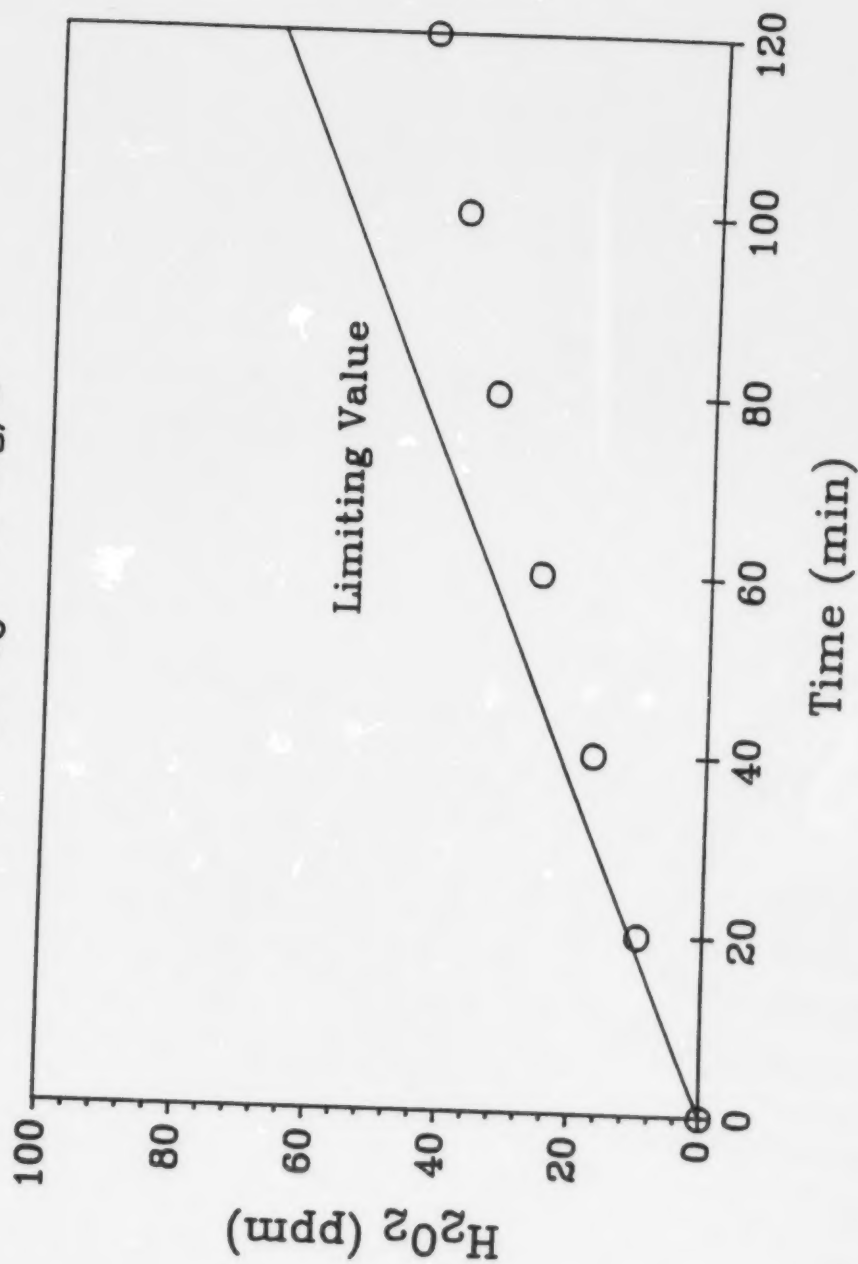


FIGURE 10

OXIDATION OF NITROBENZENE (49 - 56 PPM)

Ozone Dose: 1.0 mg/L-min

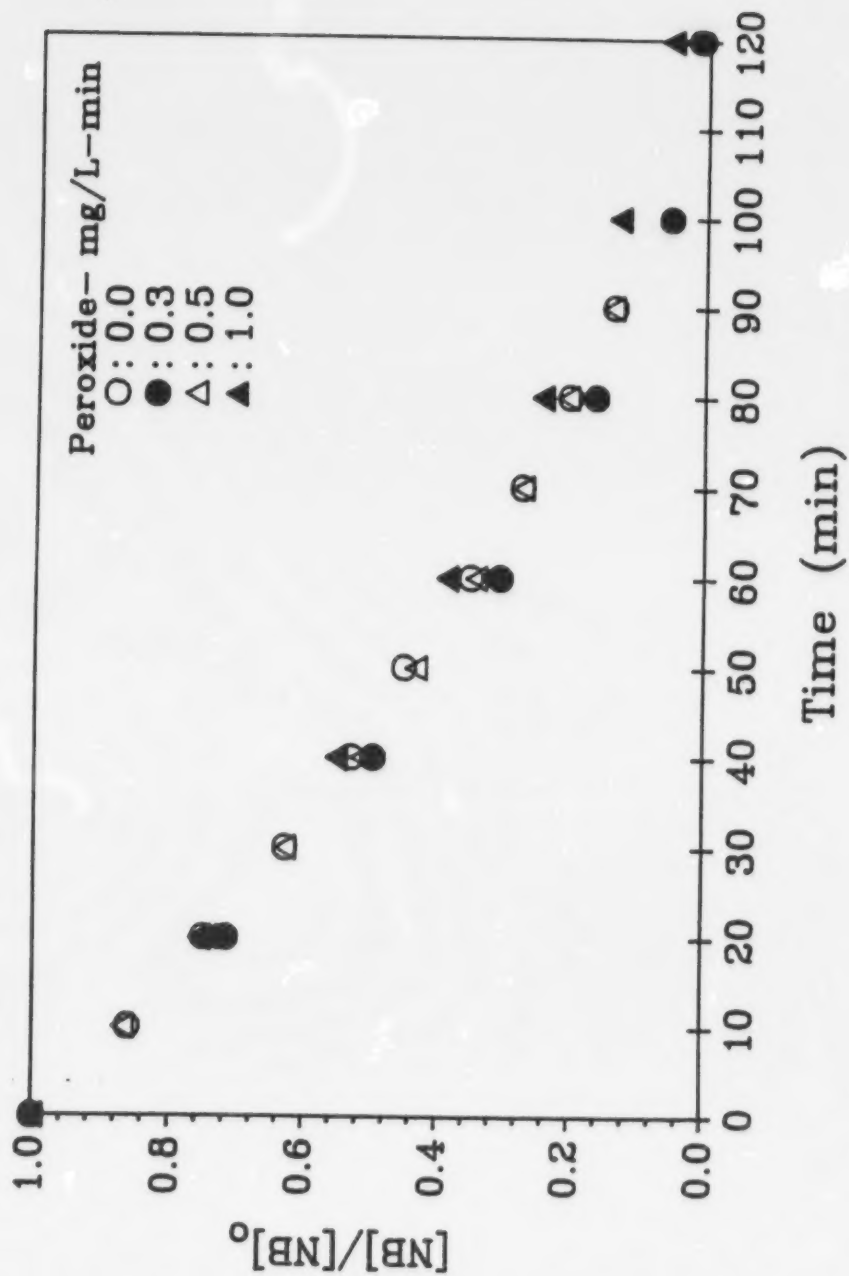


FIGURE 11

EFFECT OF BICARBONATE ON THE OXIDATION OF NITROBENZENE

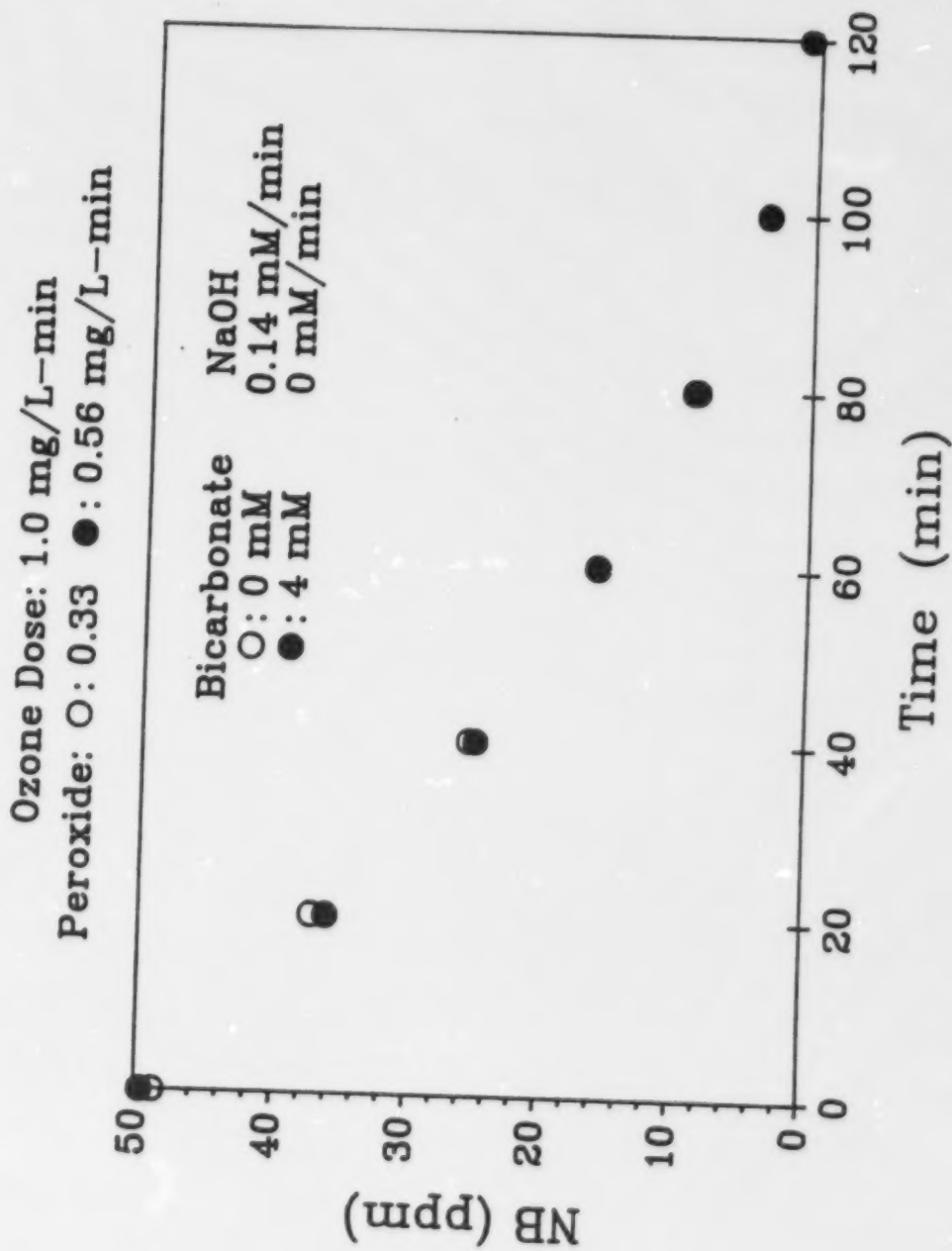


FIGURE 12

OXIDATION OF NITROBENZENE

UV Dose: 0.48 W/L

Bicarbonate: 0.1 mM

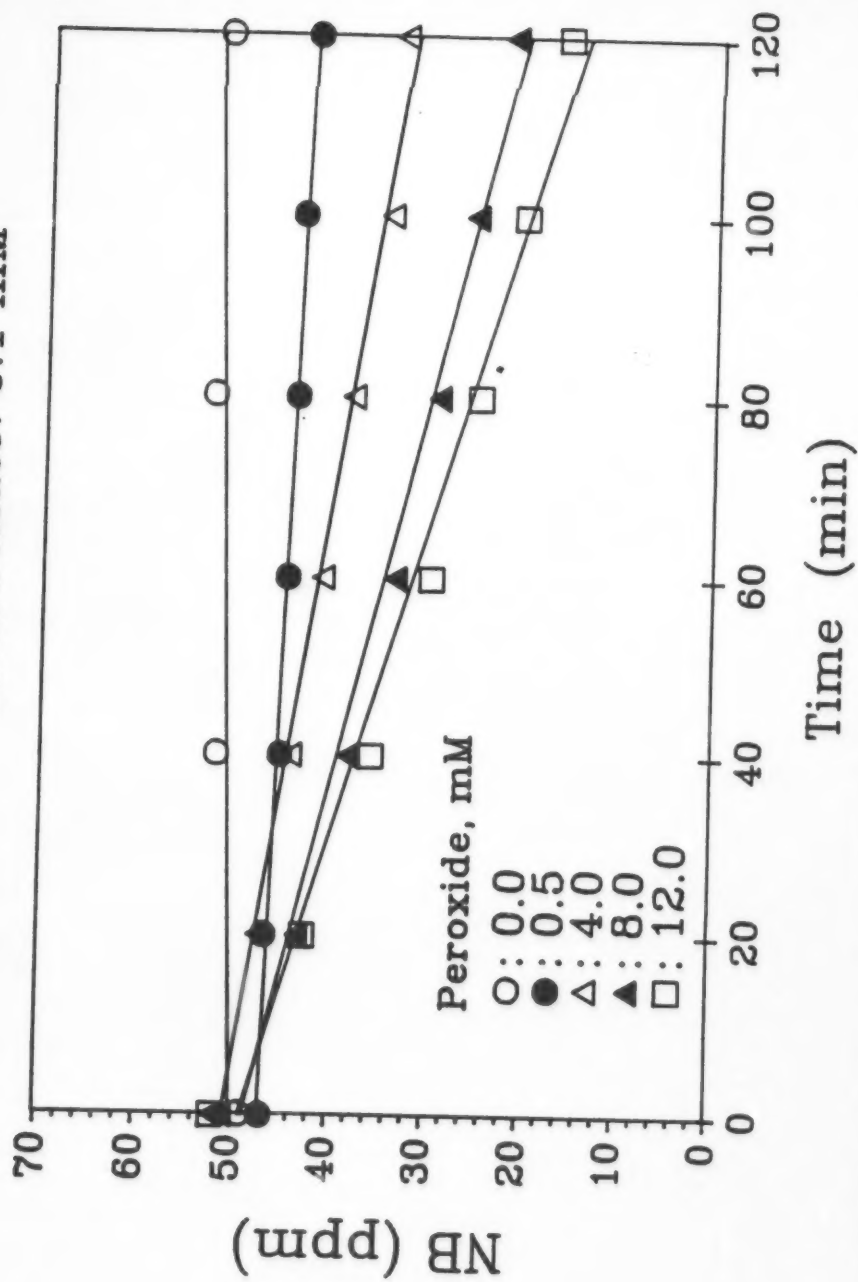


FIGURE 13

OXIDATION OF NITROBENZENE (50 PPM)

UV Dose: 0.48 W/L
Bicarbonate: 0.1 mM

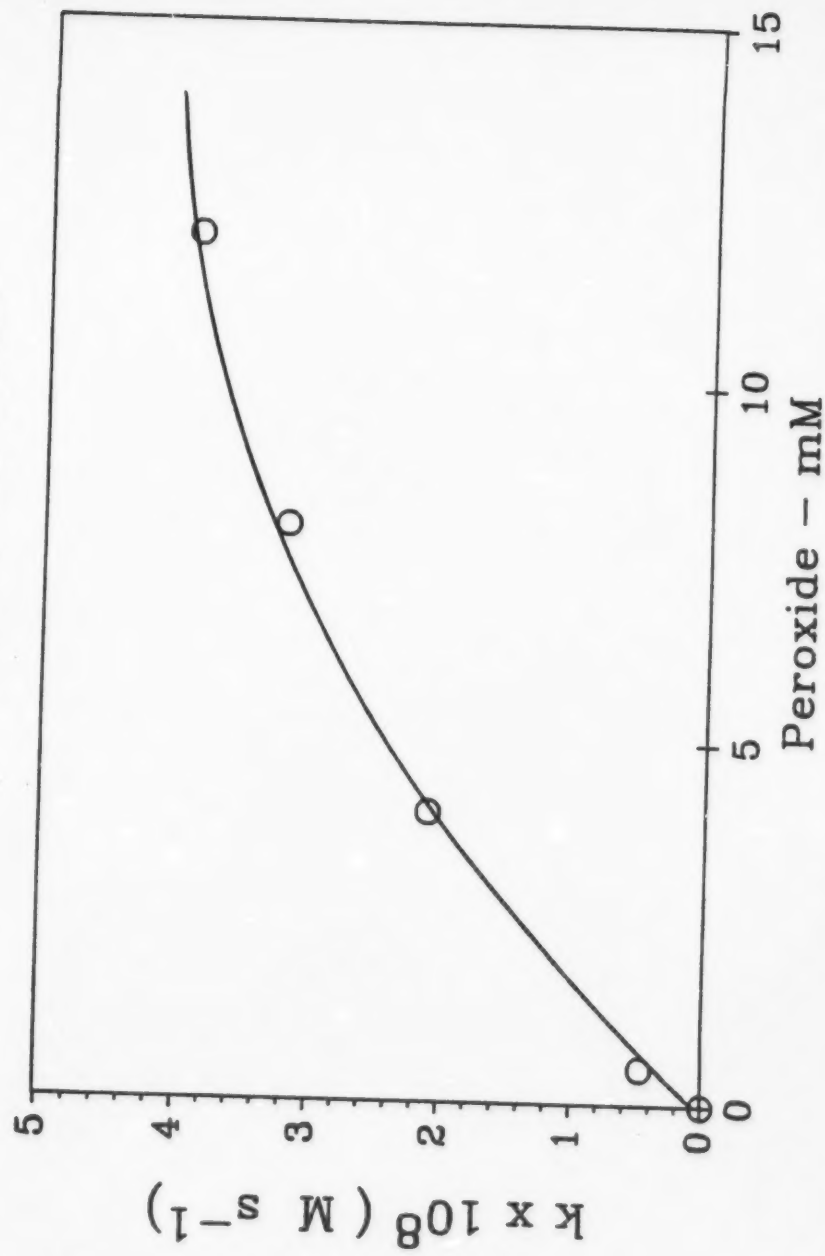


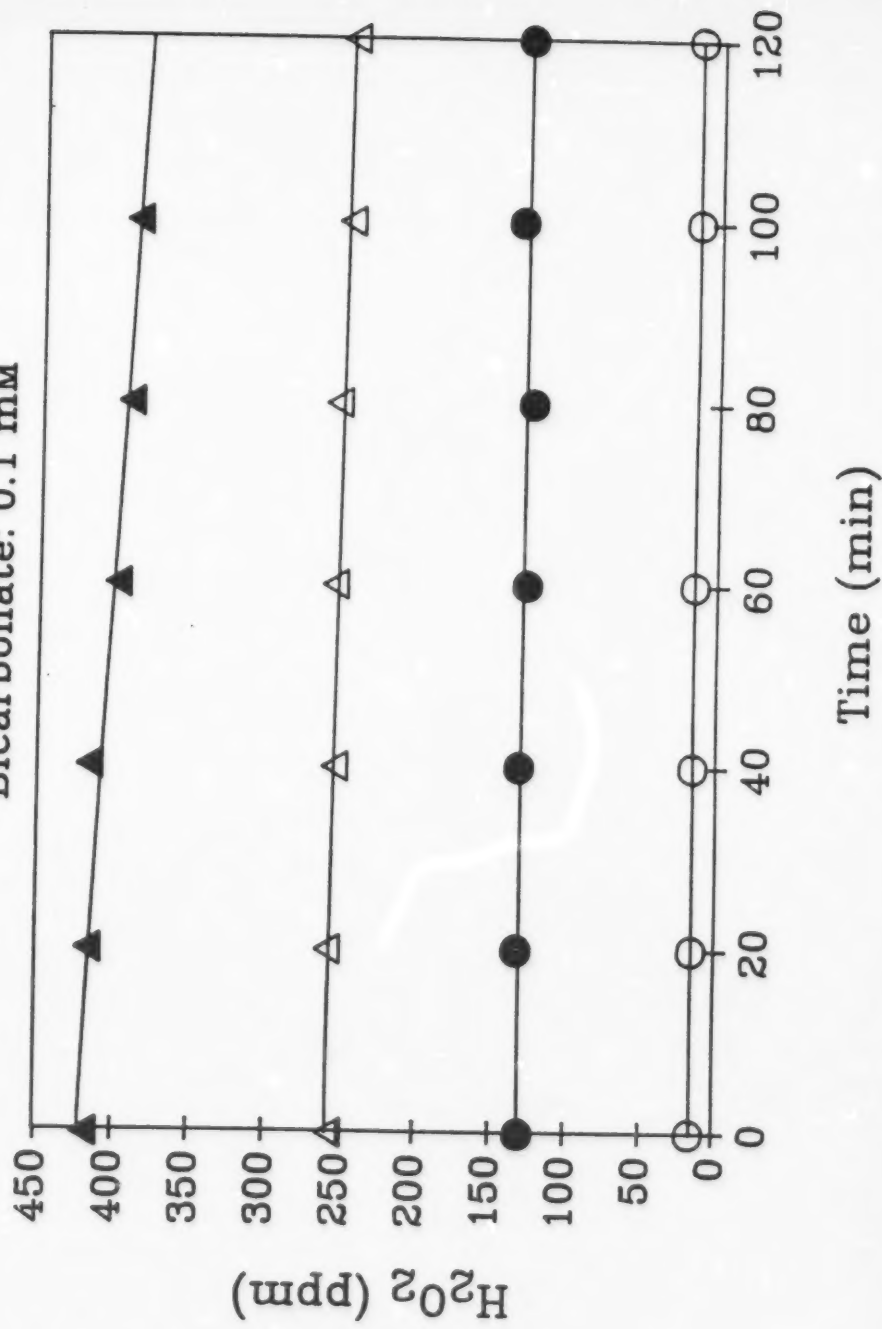
FIGURE 14

HYDROGEN PEROXIDE DECOMPOSITION

UV Dose: 0.48 W/L

$[\text{NB}]_0 = 50 \text{ ppm}$

Bicarbonate: 0.1 mM



GUIDELINES FOR THE SELECTION OF A CHEMICAL MODEL FOR ADVANCED OXIDATION PROCESSES

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ABSTRACT:

AOPs can be modeled at several different levels, depending on the amount of kinetic information and computer resources available, and the purposes to which the results will be applied. Integration of the simplified rate equations gives the most information and provides the best check of the model with actual laboratory data. Even the simplest method discussed, comparison of target compound disappearance with oxidant consumption, is considerably better for optimization purposes than is simply comparing contaminant disappearance curves between experiments run under different conditions.

INTRODUCTION

The Advanced Oxidation Processes (AOPs) are promising technologies for the treatment of water that has been contaminated with organic chemicals, because 1) these processes are capable of converting the organic contaminant completely to carbon dioxide if desired, 2) they are effective against most organic compounds, and 3) the chemicals used in the process decompose to harmless or beneficial by-products. In addition to being environmentally clean, these processes are now becoming more cost-effective than was earlier thought, because of improvements in the technology and because of the high liability now associated with discharge of contaminants to the environment. The practicality of the AOPs depends heavily on the efficiency with which the rather expensive oxidants are used. For this reason, it is important to be able to model the chemistry of the AOPs.

PURPOSES OF MODELING

There are two major purposes for which the ability to model the AOPs is valuable. The first is as a research tool to allow investigators to understand the chemistry of a particular system under study. Simple observation of the experimental variables and concentrations is generally not sufficient for an understanding of what is occurring during treatment in these complex systems. A model is required to deconvolute the subprocesses that simultaneously occur.

The second way that modeling is important is as a design tool for tailoring AOPs to a specific application. The effect that will be realized by increasing an oxidant dosage or changing a process parameter is rarely obvious, prior to actually making the change and observing the result. "More is better" frequently does not apply to the application of the AOPs. Models can be useful for estimating the effect of such a change, eliminating unproductive areas of parameter variation and suggesting potentially fruitful ones. This use is particularly important to the design engineer, who sees a potential application for an AOP but may not have the luxury of becoming completely familiar the complicated chemistry that is operative in these processes.

LEVELS OF MODELING

In the discussion that follows, concepts are phrased in terms that apply specifically to ozonation methods. The same concepts may however be adapted to simpler AOPs such as peroxide/UV.

Kinetic Methods

Complete Kinetic Description - The most detailed level of modeling that will yield much practical value is the complete kinetic description of the system. At this level, all reactions participating in the system are considered, and rate equations are written for all species. Although some use of these methods has been made (e.g., Buhler, et al, 1984; Chelkowska, 1989), the reaction systems are too cumbersome and the calculations too lengthy and complex to be of much use in other than the simplest of systems, e.g., when no organic is present. In this reaction system, important reactions take place on the sub-microsecond time scale, while "treatment" occurs on the order of tens of minutes. Integration of the resulting set of "stiff" differential equations may require 10^4 - 10^{12} steps in each of the twenty or more differential equations. Although useful as a research tool, it is doubtful that direct integration of the complete set of differential equations will see much general use. However, several useful simplifications may be made.

Simplified Kinetic Description - Several approximations are possible that greatly simplify the kinetic problem to the point that useful information can be obtained with a reasonable amount of effort. Two approaches, the steady-state approximation and the culling of kinetically unimportant reactions, are particularly useful. The steady state approximation can be used when it can be shown that the rate at which a species is produced and destroyed is much greater than the rate at which its concentration changes. This is generally true of hydroxyl radical under most treatment conditions, and is frequently true of ozonide, superoxide, organic carbon-centered radicals and peroxy radicals as well. Each time the steady state approximation is invoked for a species, its rate equation can be solved for the concentration of that species in terms of the others, and one rate equation is eliminated from the equation system.

The other important technique for simplifying the kinetic calculations is to eliminate unimportant reactions. This can only be done conditionally, that is, the reaction in question must be shown by calculation to be unimportant relative to other reactions in the system. A reaction that is unimportant under one set of conditions may be a significant contributor under other conditions. An example is the disproportion of superoxide. In ozone-containing systems, this reaction is unimportant because superoxide is consumed by the rapid reaction with ozone. However, in the peroxide/UV system, the disproportionation to hydrogen peroxide is the major superoxide sink.

The reaction system proposed for photolytic ozonation (Peyton, et al, 1987, Peyton and Glaze, 1988), shown in Figure 1, is an example of such a simplified system. This reaction scheme may also be used for ozone/peroxide by ignoring the photolysis reactions. The scheme may also be used for the peroxide/UV system by adding the superoxide/ HO_2 disproportionation reaction and ignoring the reactions involving ozone. This reaction system was arrived at by starting with the reactions proposed by Stachelin and Hoigne (1982, 1983, 1985 with Buhler) for ozone decomposition, then adding the reactions for ozone and peroxide photolysis, in addition to some other reactions from the literature. The size of this master equation list was then reduced by considering the magnitude of contribution of each reaction under water treatment conditions. The scheme shown in Figure 1 was the result of this culling of unimportant reactions, and represents a very manageable set of equations. For very dilute solutions, the reactions of hydroxyl radical with ozone and peroxide must also be included. The direct reaction of ozone with organics must also be added if appropriate.

The simplified set of differential equations can be used in at least two ways. They can be numerically integrated to describe the time evolution of species concentrations from the start of treatment to its finish. The result can be checked against experimental data for the measurable solution components, or the model can be further simplified by the introduction of adjustable parameters and comparison of calculated and experimental data used to calibrate the model. On the other hand, the rate equations may be used to calculate, for a given point during treatment, the relative importance of various competing pathways, in order to aid process optimization. The calculation will require solution species concentration data for the point in question. In a practical sense, hydroxyl radical and superoxide are impossibly difficult to measure under these conditions, but their rate equations may be eliminated from the system using the steady-state approximation, so there are still as many equations as unknowns (more correctly, unmeasurables).

"Semi-kinetic" or Partition Methods

The disparity between individual reaction rates and the time scale of the overall process of interest (i.e., treatment) can actually be used to advantage. The radical generation process can be thought of as a "black box", and the calculational problem be partitioned into two parts: the generation of hydroxyl radicals and the subsequent reactions.

RGR/Competition Method - In this method the subsequent reactions are handled by considering the division of the hydroxyl radicals between candidate reactants. The latter step is called competition kinetics and is the basis on which most new rate constants are measured. The fraction f_A of hydroxyl radicals reacting with compound A is given by

$$f_A = \frac{k_A[A]}{\sum_i k_i[C_i]} \quad (1)$$

where the k 's are second-order rate constants for the reaction of hydroxyl radicals with species A or i, $[A]$ and $[C]$ are molar concentrations, and the sum runs over all competing species, including A. The rate of disappearance of species A is then

$$R_A = f_A R_g \quad (2)$$

where R_g is the rate of radical generation. R_g can be inferred from the scheme in Figure 1 to be

$$R_s = \alpha(\dot{D}_o - R_d - R_p) \quad (3)$$

where

$$\dot{D}_o = \frac{dD_o}{dt} \quad (4)$$

and where α is the efficiency of OH production from ozone, $\dot{D}_o$ is the utilized ozone dose rate, R_d is the rate of direct ozone reaction with organics, and R_p is the rate of ozone photolysis.

RGR/Mass Balance Method - Frequently the system under study is one that can be characterized with respect to products, but the rate constants for free radical reaction of those products are not available from the literature. Under these circumstances, the total amount of OH attack on products can be determined from the sum of the removals of organic products. The reaction scheme shown in Figure 1 is quite cyclic, which suggested that a mass balance model could be derived that could be fully determined by evaluation of a small number of variables, more specifically, the concentration of measureable species in solution. The mass balance model that was derived (Peyton, et al, 1987) from Figure 1 can be applied whether HRH represents one compound or many. Important information can be obtained regarding which pathways are the major contributors to the reaction system. This information may be used to optimize processes for greater speed or efficiency.

Mass Balance Models

The mass balance model described above can be used without regard to the radical generation rate, to determine dominant reaction pathways. Once the primary reaction channels are known, further optimization can frequently be achieved by making process changes that promote those channels. For example, in the treatment of the model compound methanol by ozone/UV (Peyton, et al, 1987, and unpublished data), the dependence of the disappearance rate of methanol on the UV intensity can only be explained (within the framework of the scheme in Figure 1) by increased peroxide photolysis to hydroxyl radical. The mass balance model was used to determine the fraction of reaction proceeding by the various pathways in Figure 1. The optimization of a removal process based on that work would depend on the economic tradeoff between treatment time, ozone utilization efficiency, and the increased operation and maintenance costs associated with the use of more UV lamps.

Kinetic Probe Compound

In their discussion of the indirect (free radical) reaction of ozone with contaminants, Hoigne and Bader (1978, 1979) defined the "Oxidation Competition Value" of a water as the amount of ozone that must be decomposed to achieve a one natural log unit decrease in concentration. This quantity is an extremely useful and underutilized tool in the treatability characterization of waters for AOP treatment. It describes the extent to which the water matrix can successfully compete with contaminant for available hydroxyl radical. The general definition of the oxidation competition value, Ω_M , for contaminant M is given by

$$\ln (M/M_0) = \Delta O_3 / \Omega_M \quad (5)$$

where

$$\Omega_M = \sum_i k_i S_i / \eta' \eta'' k_M \quad (6)$$

In these equations, ΔO_3 is the amount of ozone decomposed, k_i and S_i are the hydroxyl radical rate constant and molar concentration of the various solution components that compete for hydroxyl radical, and k_M is the OH rate constant of target species M. Hoigne and Bader defined η' as the OH yield per ozone decomposed, and η'' as the "reaction efficiency", i.e., the number of OH required for reaction of one molecule of M. Thus, a plot of $\ln(M/M_0)$ versus the amount of ozone decomposed should give a straight line with slope $1/\Omega_M$.

One example of the use of this technique in our work (Peyton, LeFaivre, George, and Fleck; manuscript in preparation) has been to evaluate the ability of AOPs to remove trace contaminants in the presence of large quantities of nontarget substances. Atrazine, used as the probe compound, was spiked into a contaminated ground water at about 1 mg/L. The ground water, containing 50 mg/L of anthropogenic organic carbon, was treated with ozone/peroxide while TOC and atrazine removal were monitored. The disappearance curves are shown in Figure 2. Figure 3 shows a log plot that demonstrates four (base 10) log unit of atrazine removal during the time that about 30% of the TOC is destroyed. Another similar plot (not shown) of the natural log of the atrazine concentration versus the utilized ozone dose, D_u , yielded a value of 1.1mM for the oxidation competition value. This value can be used to calculate the rate of removal of other contaminants from the same water, provided the OH rate constant of the other contaminant is known.

Combining equations 5 and 6, and rewriting in the terminology in current useage in our group,

$$\ln(M/M_0) = \Delta O_3 / \Omega_H = \eta' \eta'' k_H \Delta O_3 / \sum k_i S_i = \alpha k_H D_u / \sum k_i S_i = \alpha k_H D_u / k' \quad (7)$$

where α (see Figure 1 and equation 3) is the efficiency of OH production from ozone (identical to Hoigne and Bader's η'), k' is the pseudo-first-order rate constant of the water matrix with hydroxyl radical, and D_u is the utilized ozone dose (not dD_u/dt , the dose rate) that is required for removal of target compound from concentration M_0 to M . The utilized dose is the applied dose minus that which appears in the off gas. Figure 3 demonstrates that the concept of a pseudo-first-order rate constant is valid, at least up to the point that the log plot deviates from linearity. Even more importantly, it demonstrates that the oxidation competition value concept, originally derived by Hoigne and Bader for more restrictive conditions, can be extended to the interpretation of semi-batch experiments with the advanced oxidation processes. Peyton (1990) has reviewed this early work of Hoigne and coworkers in more detail than is given above.

Efficiency Models

In many treatment situations, very little is known about the actual composition of the water to be treated. One approach that can be taken is to calculate and optimize the removal efficiency of a particular compound or suite of compounds, as

$$F = \Delta C / D_u \quad (8)$$

where ΔC is the amount of compound removed during the utilization of oxidant dose D_u . The utilized oxidant dose D_u is defined as

$$D_u = \int_0^t D_u \cdot dt \quad (9)$$

As in other methods, the optimum process is determined by considering the tradeoff between speed and completeness of removal and efficient oxidant utilization.

An example of the use of this method is the optimization of TOC removal from a ground water that had been contaminated by partially oxidized hydrocarbons (Peyton, LeFaivre, George, and Fleck, manuscript in preparation). A plot of the TOC removal efficiency (equation 8) versus

degree of conversion (mineralization) of organic carbon is shown in Figure 4 for ozone/peroxide treatment at pH 9, ozone/UV treatment at pH 3. The efficiency was seen to be high for ozone/peroxide and low for ozone/UV in the early part of the reaction, while the reverse is true in the later stages. These results suggested a two-stage process using ozone/peroxide in the first stage, followed by pH adjustment and ozone/UV in the second. The curve corresponding to that experiment shows an overall increase by a factor of two in the oxidant utilization efficiency of the two-staged process, over that of the individual processes. This increase in efficiency was not obvious from the simple disappearance curves, shown in Figure 5.

GUIDELINES FOR MODEL SELECTION

Having defined levels of modeling, the guidelines for model selection become fairly obvious. The constraints are 1) the amount of kinetic information available, such as solution species identities and concentrations, and appropriate rate constants; 2) the computing resources available, including computer speed and memory, and programming capability, 3) the use to which the results will be applied.

Where complete kinetic information is available, the simplified kinetic approach yields the most information while still being practical. This is the most desirable level of modeling for research applications. It frequently requires relatively powerful personal computers or mainframe machines.

The RGR/competition method requires almost as much kinetic information, but less computer resources. Programs are simpler. In some cases the significance of the results is easier to grasp since the partition of the radicals between species is obvious. That data can of course also be obtained from the kinetic method, but requires additional programming since that information is not generated in the normal course of the calculation. This method is also easy to use to for an "instantaneous" calculation, i.e., at a selected point during treatment, and can easily be done by hand.

The RGR/mass balance method can be used in the more common situation where a lot is known about solution species and degradation pathways, but the necessary rate constants are not available. Most investigators will find it inconvenient to evaluate the required rate constants experimentally. The computing effort is similar to the RGR/competition method.

The Mass Balance model is used when the radical generation rate is not known, or when other information such as reaction pathways is to be inferred from concentration data. This method requires minimal knowledge of rate constants.

The kinetic probe model is used to characterize the water with respect to treatability, and requires only the knowledge of the rate constant of the probe compound, in addition to experimental data on the target compound disappearance and utilized ozone dose.

Finally, the efficiency model is the easiest to use and can be tailored to individual situations and objectives. It is much better than simple disappearance curves for the analysis of treatability data, but requires the measurement of the utilized ozone dose.

ACKNOWLEDGEMENT

Examples have been liberally quoted from the work of Michelle Smith, Brent Peyton, and Mike Fleck in the oxidation research group at the Illinois State Water Survey.

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Figure 1: Reaction pathways in the Advanced Oxidation Processes that use ozone. Greek symbols are efficiencies of the various steps.

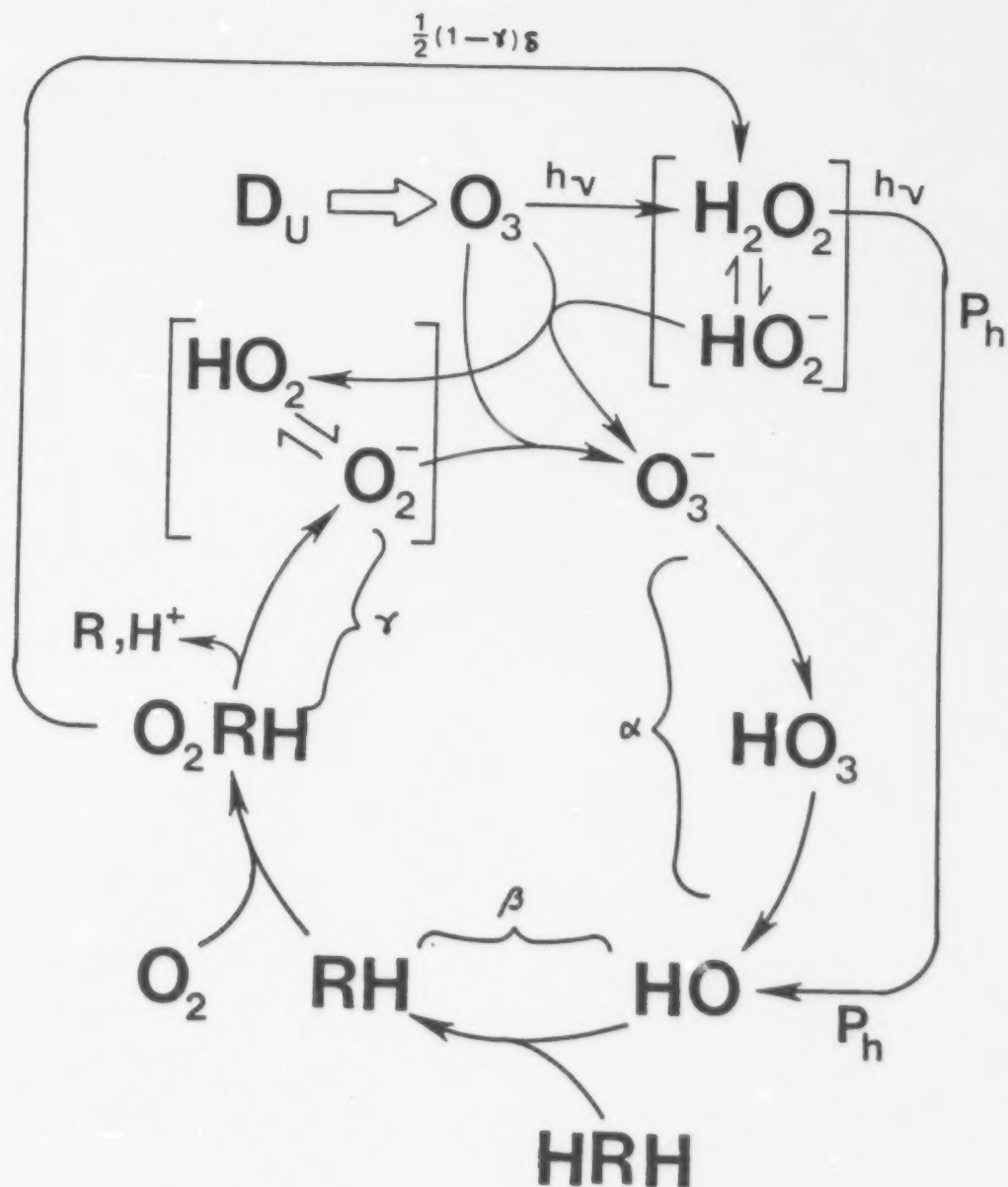


Figure 2: Destruction of atrazine in the presence of 50 mg/L of organic carbon. Initial atrazine concentration was 0.9 mg/L.

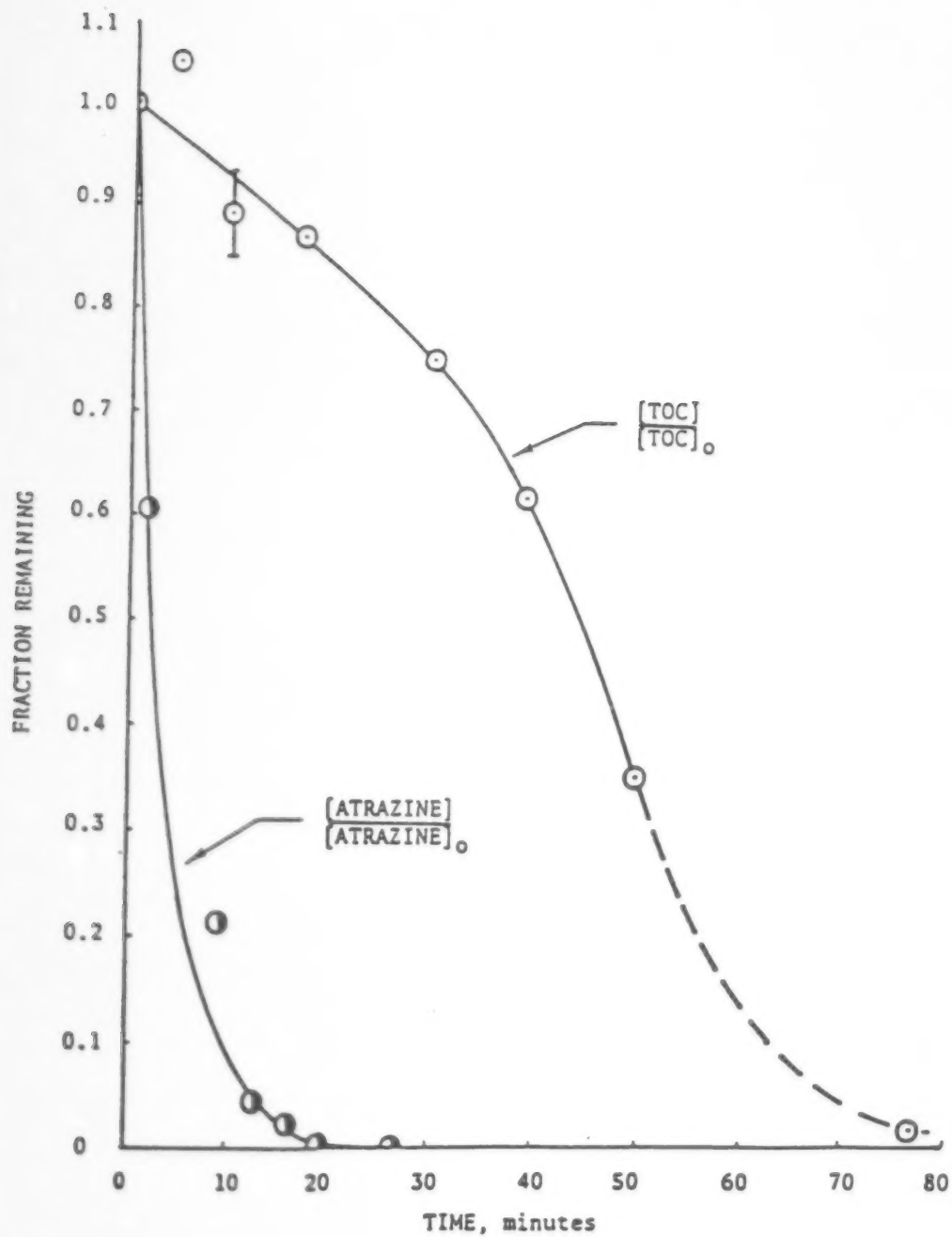


Figure 3: Pseudo-first-order plot of atrazine removal by ozone/peroxide.

DESTRUCTION OF ATRAZINE IN CONTAMINATED GROUND WATER
USING ADVANCED OXIDATION PROCESSES

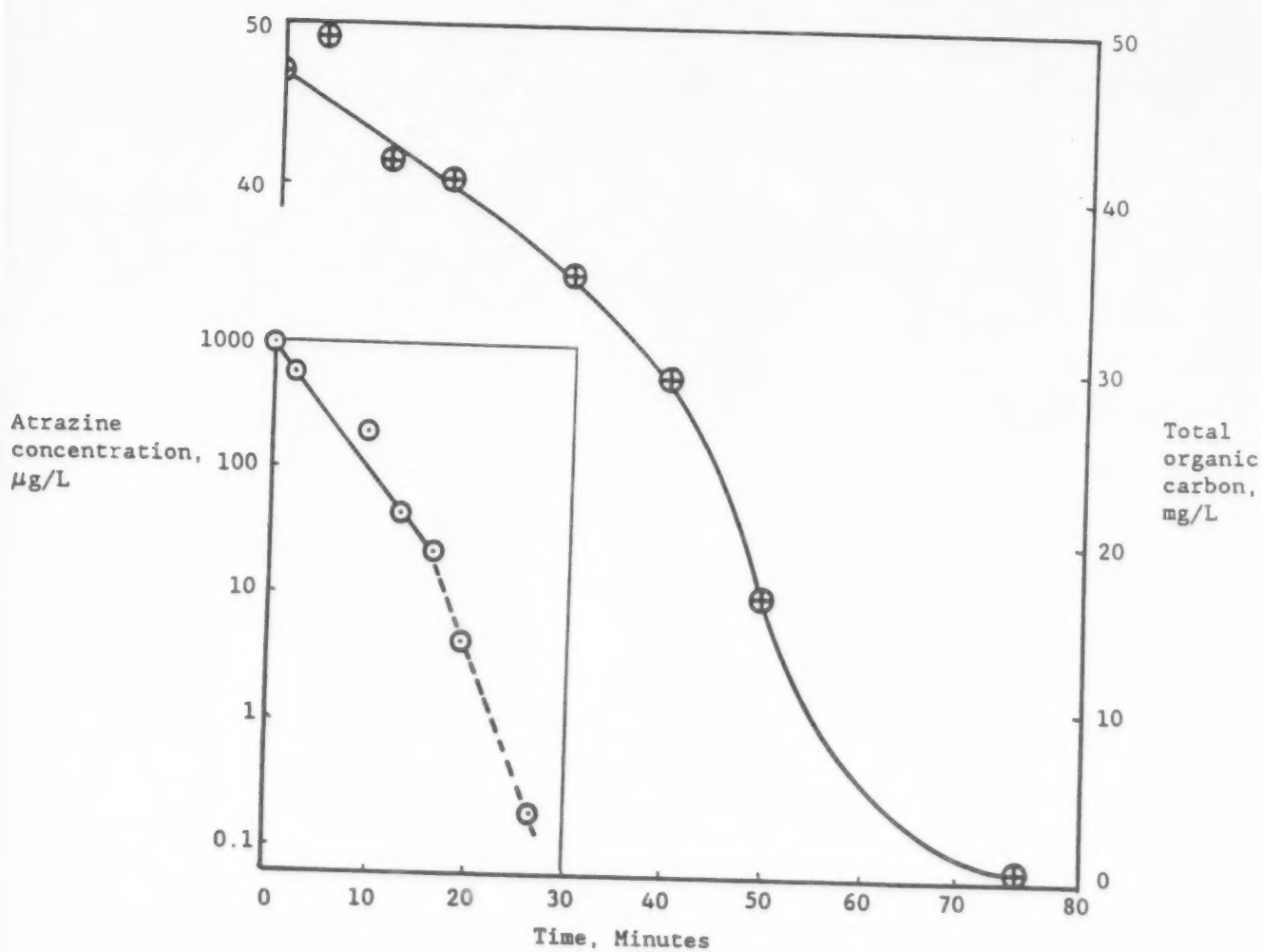


Figure 4: Comparison of efficiency of AOPs for TOC destruction.

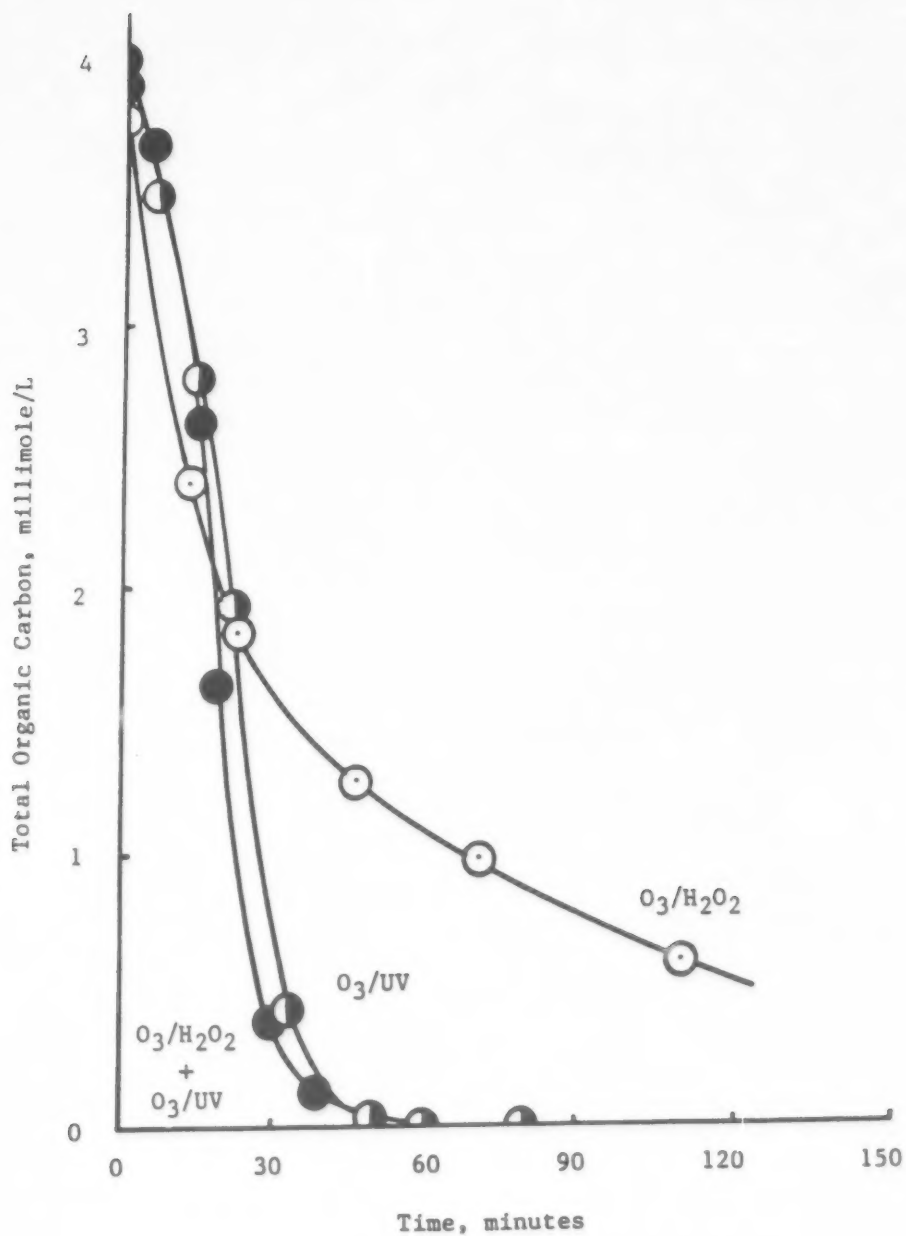
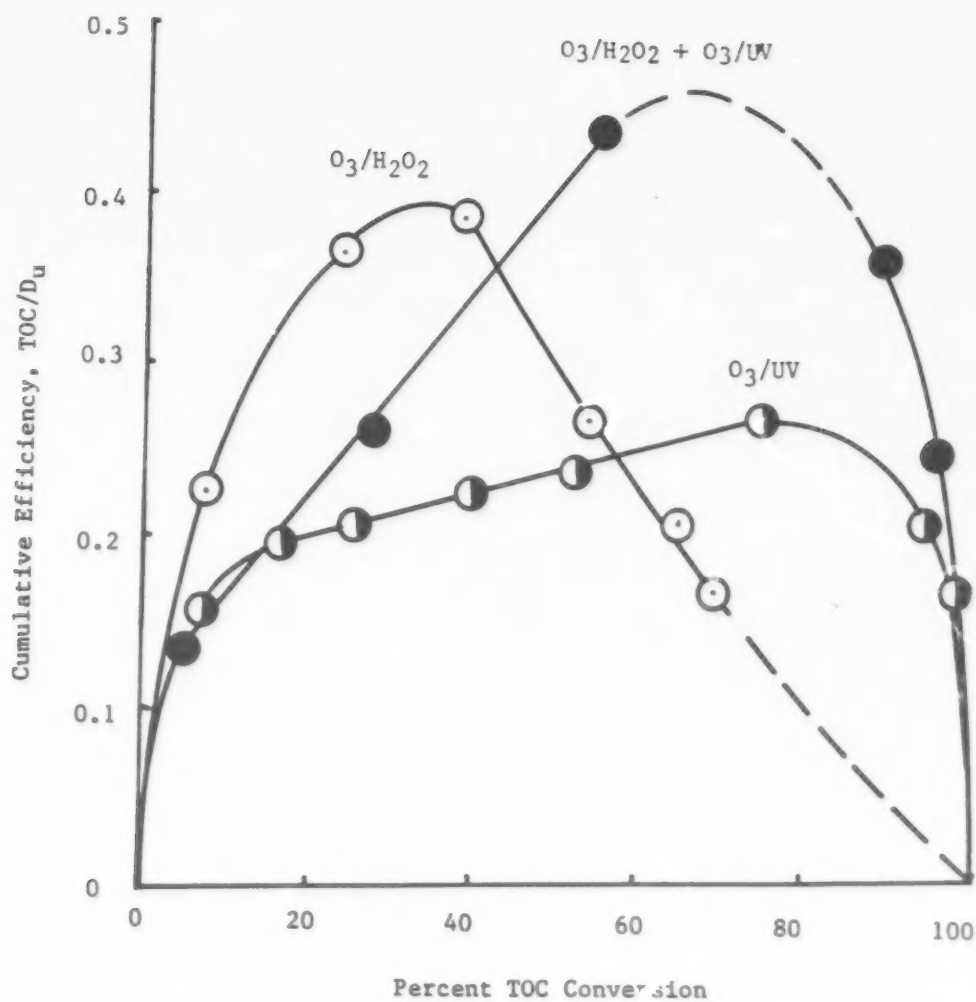


Figure 5: Comparison of disappearance curves for TOC removal by AOPs



**PURIFICATION AND DISINFECTION OF WATER
BY ULTRAVIOLET LIGHT AND HYDROGEN PEROXIDE**

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ABSTRACT:

This project investigated the destruction of organic compounds and microorganisms in water by ultraviolet catalyzed oxidation using hydrogen peroxide as the oxidizing agent. The combination of UV light and hydrogen peroxide was effective in decomposing all of the organic compounds studied. The rates of destruction increased with increasing peroxide concentration and UV light intensity, and were highly dependent on chemical structure. The aromatic compounds formed many intermediates that could be eliminated by extending the treatment time. The destruction of mixtures of organic compounds showed strong interactions between reacting components. The inactivation of E. coli and B. subtilis spores by UV light and/or hydrogen peroxide was studied in flat plate reactors. By using thin liquid films, the combination of UV light and peroxide greatly increased the rates of inactivation of both microorganisms. The results were correlated by a mixed second order kinetic model.

INTRODUCTION:

The removal of low levels of toxic and hazardous organic compounds from water can be a difficult and costly task. Conventional treatment methods such as aeration and carbon adsorption are ineffective with certain types of compounds. Both techniques are also non-destructive unless combined with other treatment methods.

Advanced oxidation processes using ozone or hydrogen peroxide with ultraviolet light have proven effective for the destruction of many organic compounds in water (1-7). The photochemical action of UV light on ozone or peroxide produces hydroxyl radicals and other reactive species that attack the organic molecules. Advantages of hydrogen peroxide include storage for use according to process demand, ease of mixing with water, and costs that are less sensitive to scale of operation than ozone.

The main purpose of this project was to investigate the destruction of typical aliphatic and aromatic compounds in water by the UV/peroxide process. In addition, the disinfection of water by UV light and hydrogen peroxide was examined.

EXPERIMENTAL METHODS

The experiments were conducted in a variety of batch and flow reactor systems. Most of the studies on aliphatic compounds and mixtures were made in a batch photochemical reactor with an inside diameter of 7.5 cm, a length of 30 cm and a total volume of about 1.5 litre (4). An ultraviolet lamp emitting about 2 watts at 254 nm was centrally located inside the reactor. The aromatic research was conducted in a recirculating flow reactor consisting of concentric quartz tubes with inner and outer diameters of 2.5 cm and 5.4 cm (5). An ultraviolet lamp emitting about 5.3 watts at 254 nm was located within the inner tube. The UV light passed radially through the annular region containing the circulating liquid.

Disinfection studies were made in circular flat plate reactors with diameters of 15 cm and 10 cm. The reactors were irradiated from above by a UV lamp emitting about 3.6 watts at 254 nm.

RESULTS AND DISCUSSION

Single Components:

The synergistic effect of hydrogen peroxide and UV light on the destruction of benzene is shown in Figure 1. Hydrogen peroxide alone did not decompose benzene but UV light alone reduced benzene concentration by about 50% in 90 min. The combination of hydrogen peroxide and UV light was much more effective than either alone, with over 98% removal of the benzene in 90 min.

The concentration of hydrogen peroxide and intensity of UV light had the largest effects on the rates of reaction. Figure 2 shows the effect of initial hydrogen peroxide to benzene molar ratio on the rate of disappearance of benzene. As the peroxide concentration is increased, more hydroxyl radicals are available to attack the benzene molecules.

Comparisons of the rates of reaction of aromatic and aliphatic compounds are shown in Figures 3 and 4. For the aromatic compounds studied, apparent first order rate constants varied only by a factor of about 2. Rates of reaction for the aliphatic compounds differed

greatly, with apparent first order rate constants differing by a factor of about 20. Chlorinated aliphatics with carbon to carbon double bonds degraded much faster than structures with single bonds.

Reaction Products:

When aromatic compounds were treated with hydrogen peroxide and UV light, the absorbances of the solution at 254 nm increased rapidly with time, reached a maximum, and then decreased to a negligible value (Figure 5). The maximum absorbances occurred at times where most of the benzene and phenol had reacted. The increase in absorbance is caused by the formation of reaction intermediates that absorb UV light more strongly than the parent compounds. These reaction intermediates may be as harmful to the environment as the original aromatic compound. By adding sufficient hydrogen peroxide and extending treatment time, the absorbing compounds can be eliminated. Analyses of selected compounds by HPLC and GC/MS confirmed the formation and destruction of several intermediates.

With the chlorinated aliphatic compounds, the concentrations of chloride ion were measured during the runs. For the compounds studied, essentially quantitative conversion of the reacted chlorine to chloride ion was achieved, indicating that the chlorinated structures were effectively destroyed.

Mixtures:

Benzene and trichloroethylene were selected for mixture studies since they are common priority pollutants and differ greatly in properties. The concentrations in the mixtures ranged from 0.05 to 0.2 mM for benzene and from 0.15 to 0.6 mM for trichloroethylene, which gave the same range of organic carbon concentrations for each component (0.3 to 1.2 mM).

Figure 6 compares apparent first order rate constants for 0.2 mM benzene alone, 0.6 mM trichloroethylene alone, and a mixture with 0.1 mM benzene and 0.3 mM trichloroethylene. Each of these solutions initially contained 1.2 mM organic carbon concentration. The rate constant for benzene alone was similar in magnitude to that for benzene in a mixture, but the rate constant for trichloroethylene in a mixture was about one-half of its value as a pure component.

The results of this study show that the aromatic component, benzene, greatly retarded the rate of destruction of the aliphatic component, trichloroethylene. The strong interaction between

components demonstrates the need to study actual mixtures experimentally instead of extrapolating pure component data.

Disinfection:

The inactivation of microorganisms by UV light and hydrogen peroxide was studied in circular flat plate reactors irradiated from above. The microorganisms were E. coli (ATCC 23716) and B. subtilis spores (ATCC 6633 and 9372) at initial concentrations from 1×10^6 to 3×10^6 species/ml. Although many studies have been reported on disinfection by UV or peroxide alone, the combination has received little attention (8, 9, 10).

The effect of UV alone on inactivation of the three microorganisms is shown in Figure 7. The B. subtilis 9372 spores were the most resistant to UV light and were emphasized in this study. With hydrogen peroxide alone, high concentrations were needed to destroy the organisms in reasonable times. The B. subtilis 9372 spores, for example, required 14 min. in 10 wt % peroxide for 99% inactivation.

Initial experiments with both UV light and hydrogen peroxide were conducted in a 15 cm diameter reactor with a liquid depth of 25 mm. As the concentration of peroxide was increased, the rate of inactivation decreased.

To explain this apparent negative effect of peroxide, the absorbance of UV light by peroxide was calculated from the Beer-Lambert law. With 0.5% peroxide and $90 \mu\text{W}/\text{cm}^2$ incident intensity, the calculated average intensities in the reactor were $5 \mu\text{W}/\text{cm}^2$ for 25 mm depth, $39 \mu\text{W}/\text{cm}^2$ for 3 mm depth and $81 \mu\text{W}/\text{cm}^2$ for 0.3 mm depth. Thus, to reduce the effects of peroxide absorption on rates, thin liquid films are required.

The effect of hydrogen peroxide concentration on destruction of B. subtilis 9372 spores in a 10 cm reactor with 0.3 mm liquid depth is shown in Figure 8. The presence of peroxide greatly enhanced the rates of inactivation up to 0.5% hydrogen peroxide. The rate declined above 0.5% because of UV light absorption by the peroxide.

The data were fit to mixed second order and series event kinetic models (11). The series event model assumes that multiple events (hits) are needed to reach a threshold level for

inactivation. The mixed second order model assumes that a single hit will inactivate an organism and that the number of hits is proportional to the UV dose:

$$-dN/dt = kIN$$

N = surviving organisms, no./cm³

I = UV light intensity, $\mu\text{W}/\text{cm}^2$

t = irradiation time, s

The mixed second order model was superior to the series event model for the runs with both UV and peroxide. The rate constant, k , ranged from $0.78 \times 10^{-4} \text{ cm}^2/\mu\text{W s}$ for UV only to $4.3 \times 10^{-4} \text{ cm}^2/\mu\text{W s}$ for UV plus 0.5% peroxide.

For a given light intensity, the optimum peroxide concentration increases with decreasing liquid depth. The results suggest the need for thin film reactors when disinfecting with UV light and hydrogen peroxide.

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Figure 1: Effect of H_2O_2 alone, UV alone, and H_2O_2 plus UV on decomposition of benzene in recirculating flow reactor. Initial benzene = 0.2 mM. Initial H_2O_2 = 1.3 mM.

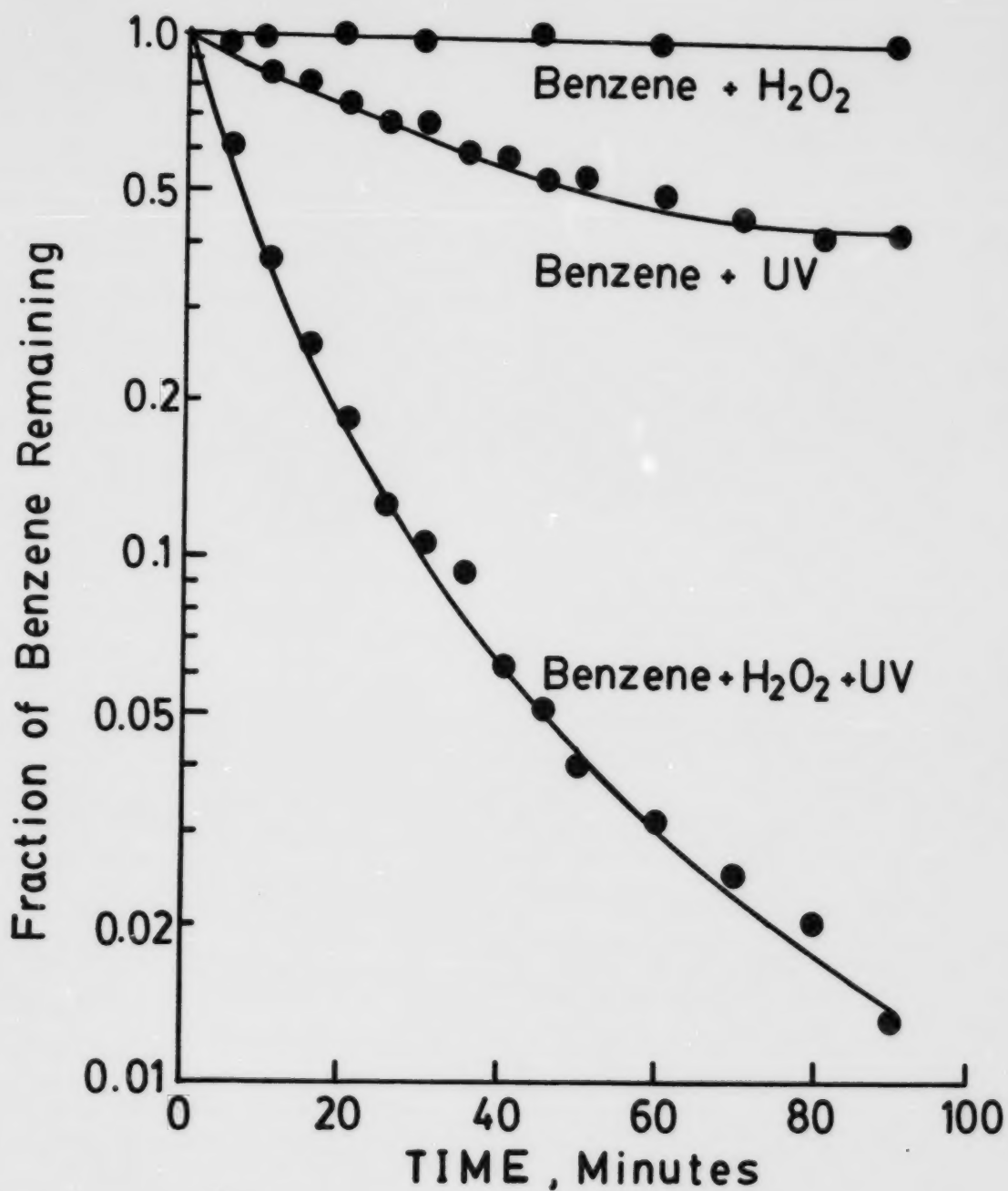


Figure 2: Effect of initial molar ratio of H_2O_2 to benzene on decomposition of benzene in recirculating flow reactor. Initial benzene = 0.2 mM.

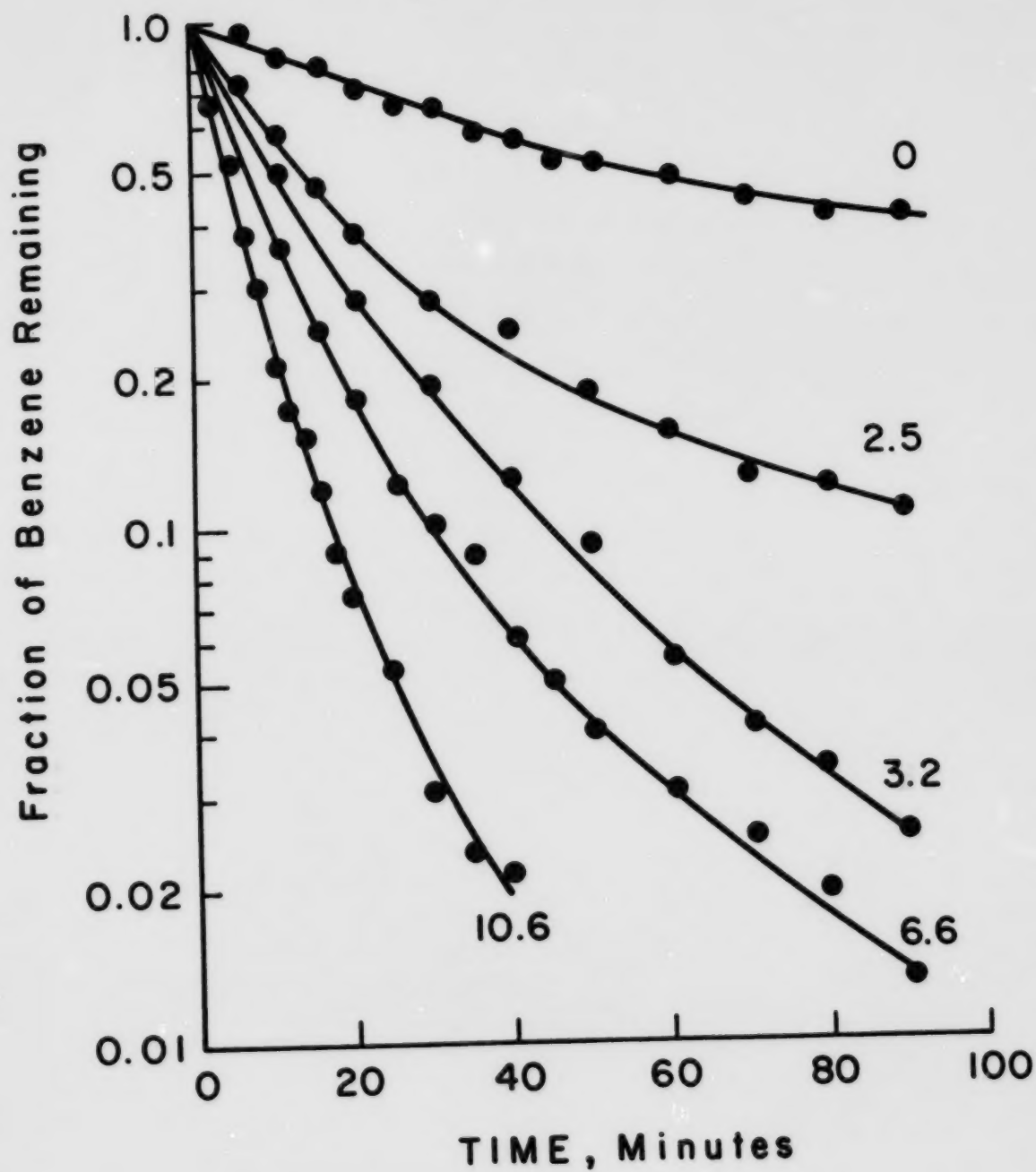


Figure 3: Comparison of rates of reaction of aromatic compounds in recirculating flow reactor. Initial pollutant = 0.2 mM. Initial H_2O_2 = 1.4 mM.

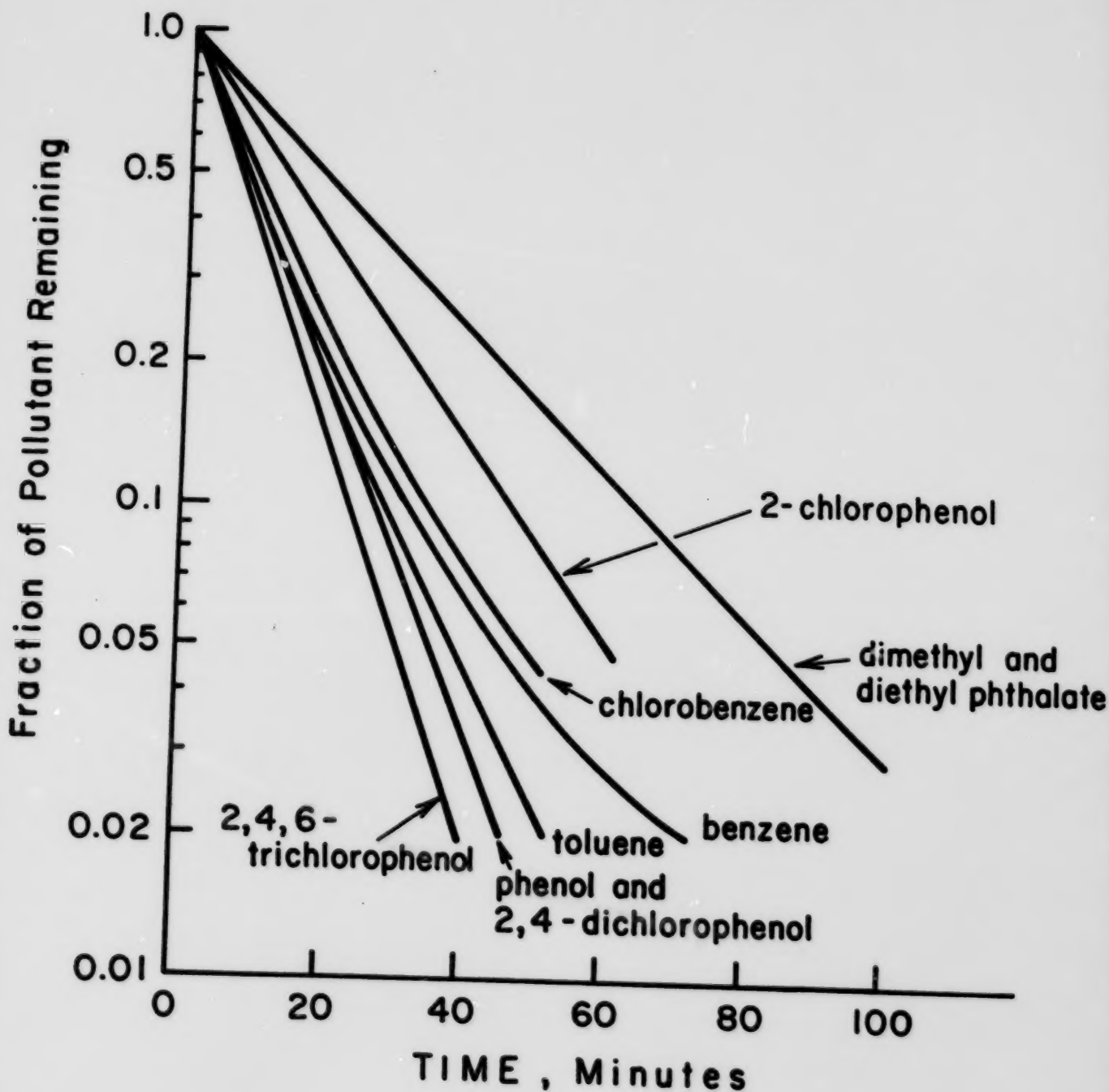


Figure 4: Comparison of rates of reaction of halogenated aliphatic compounds in batch reactor. Initial pollutant = 50 - 100 ppm.

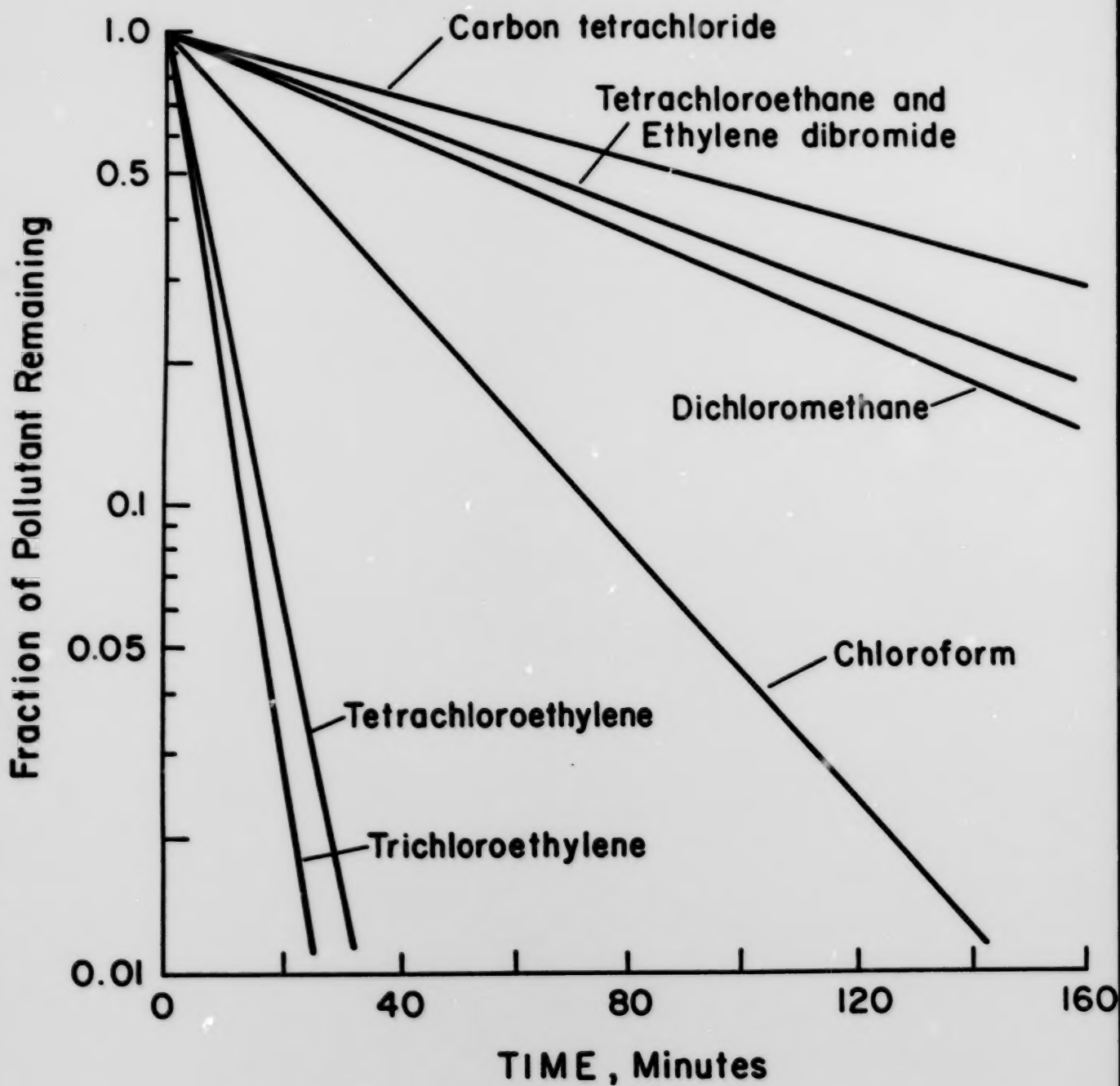


Figure 5: Change of absorbance at 254 nm with reaction time. Initial pollutant = 0.2 mM.
Initial H_2O_2 = 1.4 mM.

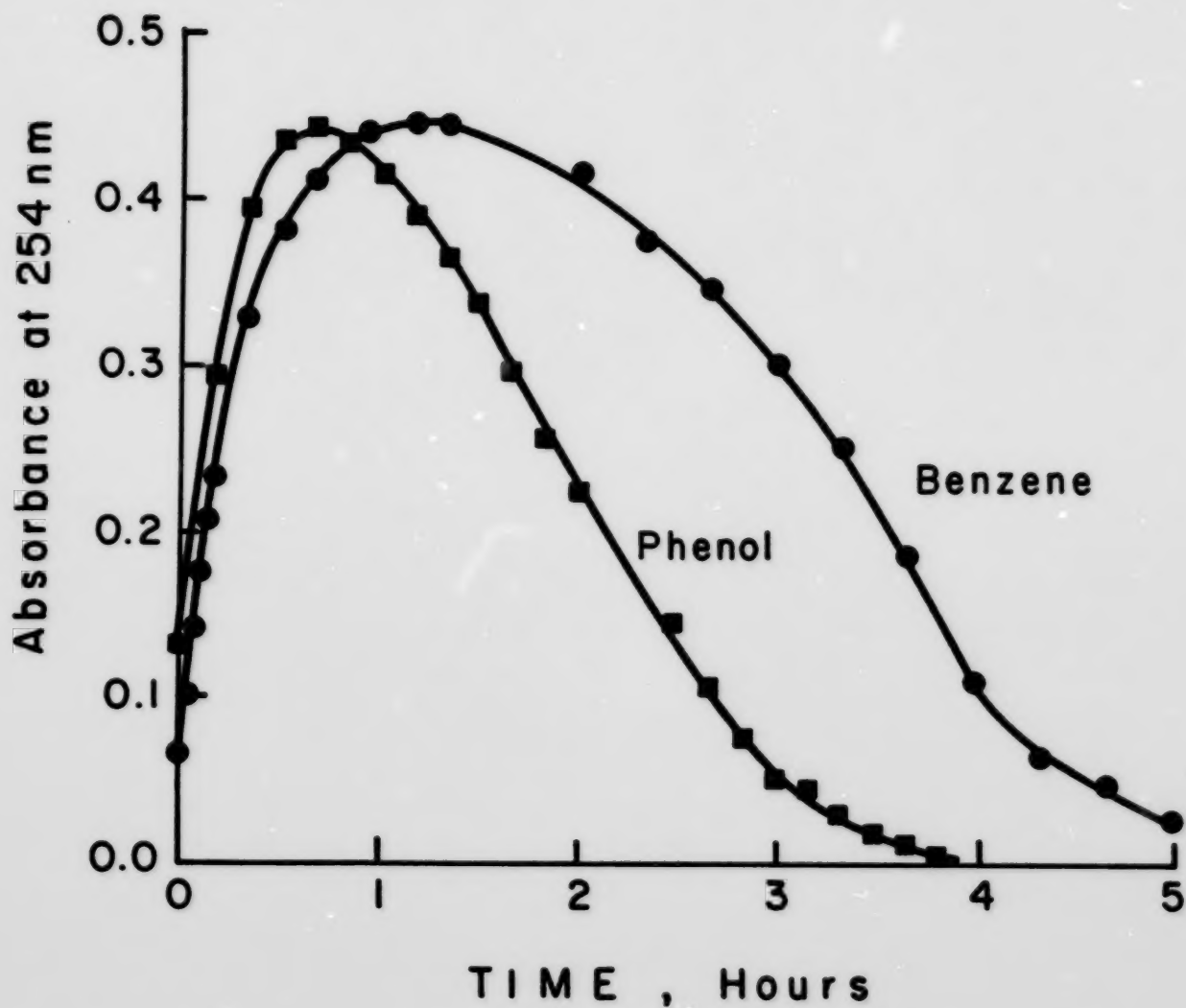


Figure 6: Comparison of apparent first order rate constants for 0.2 mM benzene alone, 0.6 mM trichloroethylene alone, and a mixture with 0.1 mM benzene and 0.3 mM trichloroethylene. Initial $\text{H}_2\text{O}_2 = 1.8 \text{ mM}$.

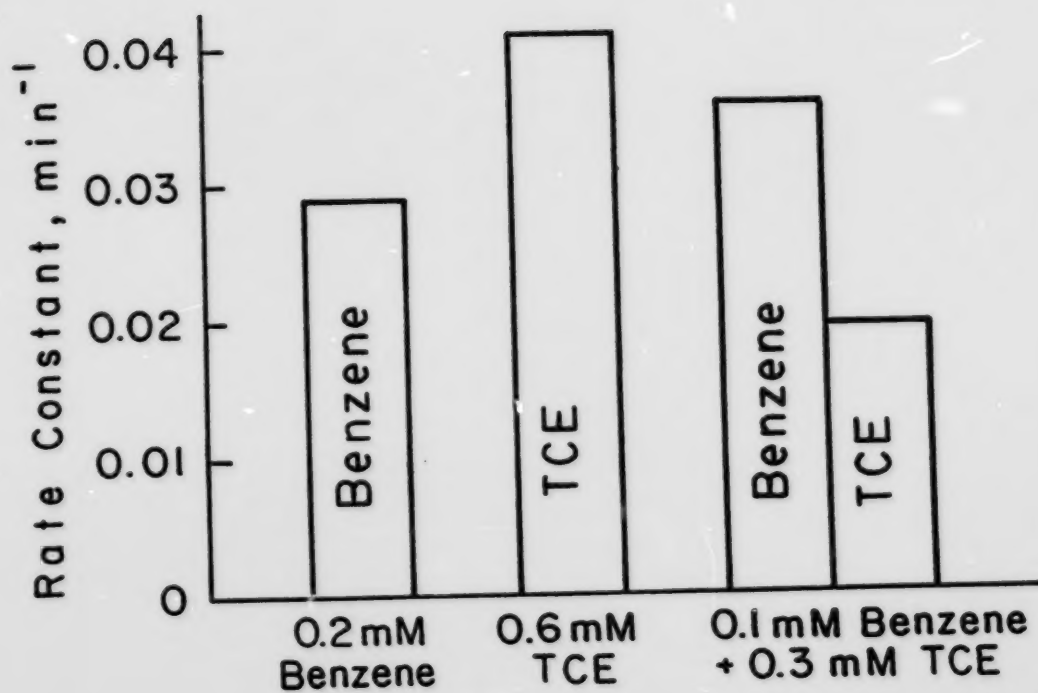


Figure 7: Effect of UV light only on inactivation of *E. coli* and *B. subtilis* in batch reactor. UV intensity = $90 \mu\text{W}/\text{cm}^2$.

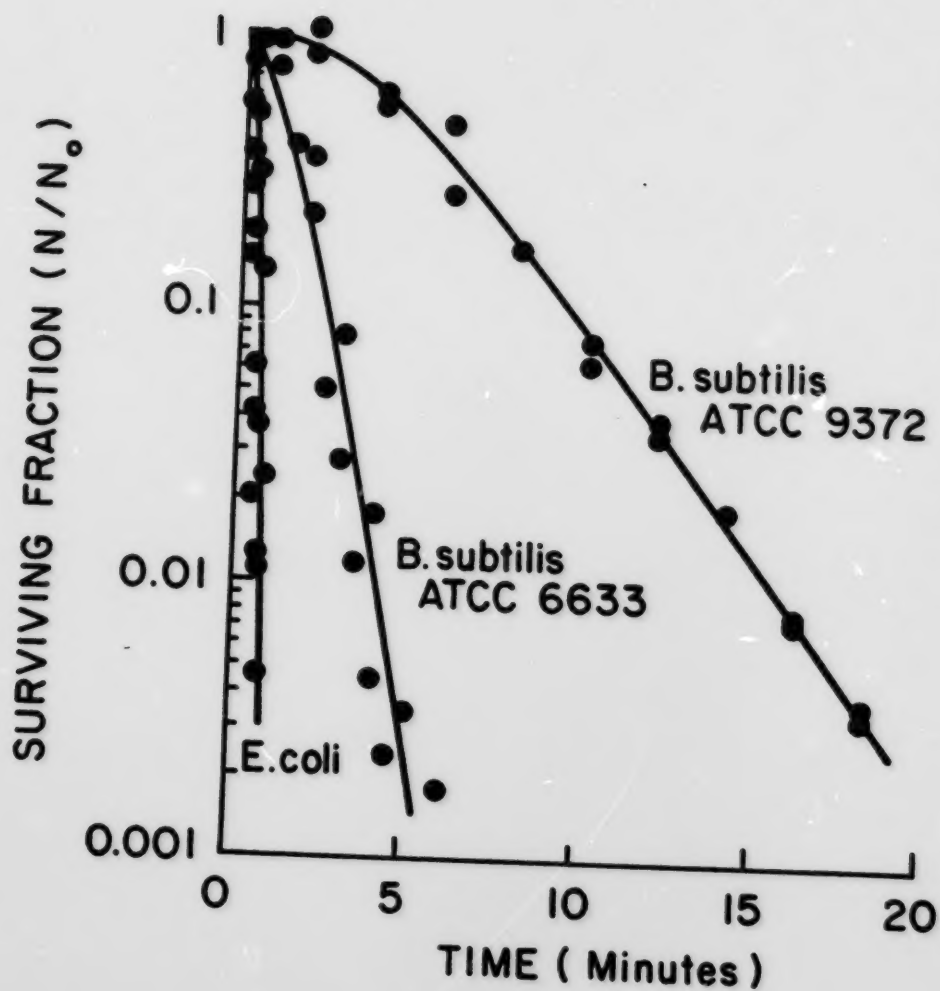
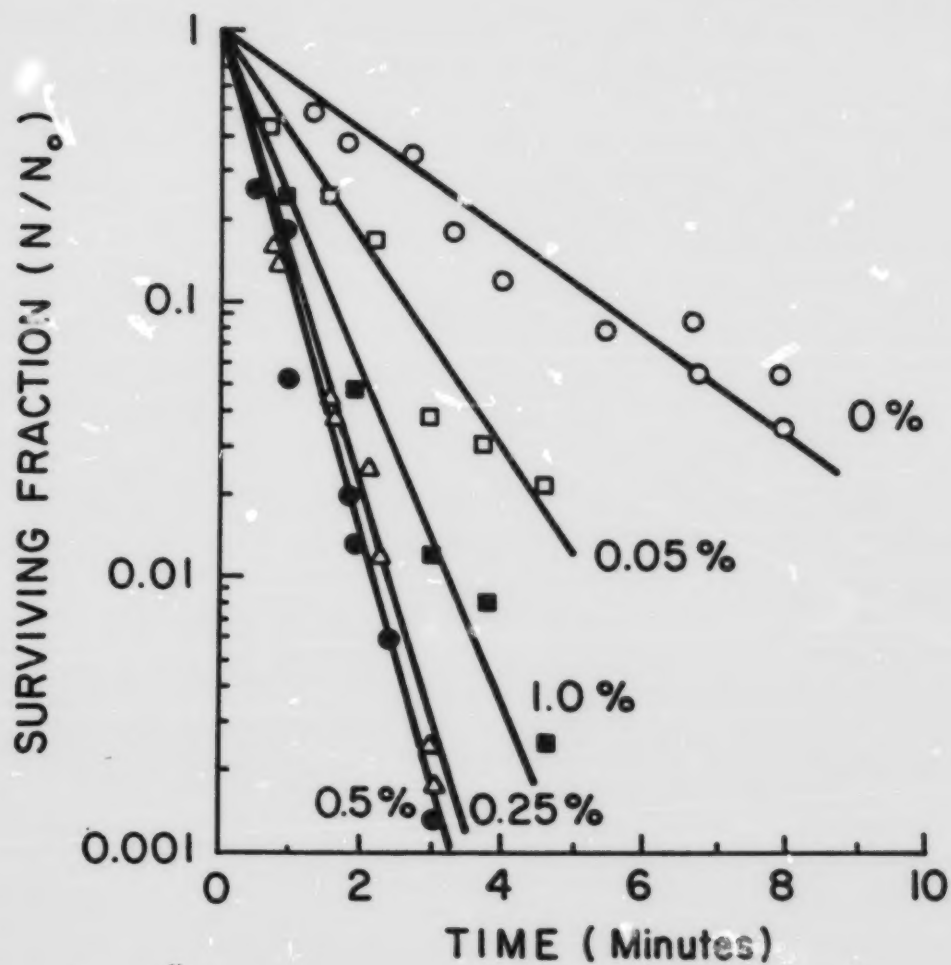


Figure 8: Effect of UV light and H_2O_2 concentration on inactivation of *B. subtilis* 9372 spores. Liquid depth = 0.3 mm. UV intensity = $90 \mu W/cm^2$. Lines predicted by mixed second order kinetic model.



**HIGH-ENERGY ELECTRON BEAM IRRADIATION:
AN ADVANCED OXIDATION PROCESS FOR THE TREATMENT OF
AQUEOUS BASED ORGANIC HAZARDOUS WASTES**

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ABSTRACT:

The use of high-energy electrons for the treatment of aqueous solutions appears to be a very promising approach to solving numerous problems associated with contaminated water. Irradiation of aqueous solutions results in the formation of free radicals, e^-_{aq} , $H^\cdot$, and $OH^\cdot$. The stable oxidant formed during irradiation is H_2O_2 . In aqueous solutions of contaminants, the free radicals react with these contaminants and at high doses oxidize them to CO_2 , H_2O and salts. Reaction mechanisms for the compounds studied predict that incomplete oxidation results in the formation of low molecular weight organic aldehydes and acids. The study reported in this paper utilizes a pilot plant capable of treating 120 gpm. The accelerating voltage of the electron accelerator is 1.5 MeV with variable current of up to 50 Ma. Influent streams of potable water, and raw and secondary wastewater have been used for this study. The compounds which have been studied to date include halogenated methanes, ethanes, ethenes, propanes and butadiene, benzene and substituted benzenes, phenols and dieldrin. Removal efficiencies range from 85 to, in most cases, > 99%.

INTRODUCTION:

Groundwater, used as a source for drinking water, has been shown to be contaminated in many areas of the country and world. The contaminants of interest in this paper are organic compounds, many of which may persist for considerable periods in the subsurface environment. Because of this contamination and the recalcitrant nature of many of the chemicals, it is of interest to develop processes which will effectively and efficiently remove

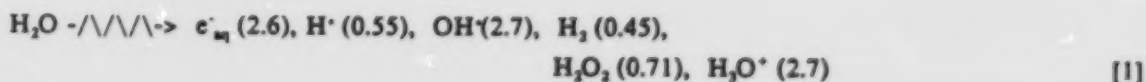
these compounds from aqueous solutions. Contaminated groundwater often contains the organic solutes at relatively low concentration which places constraints upon the removal of these compounds, in particular where equilibrium processes are involved. This study focuses upon the results using high-energy electron irradiation of aqueous solutions for the removal of organic solutes at low concentrations, i.e. less than a mg L⁻¹. Table 1 outlines the most frequently found hazardous chemicals at Superfund sites in the US. Many of the organic compounds on this list have been studied using high-energy electron beam irradiation and these compounds will be the focus of this paper.

RADIATION CHEMISTRY OF NATURAL WATERS:

The purpose of this section is to provide an overview of radiation chemistry. This brief introduction should assist the reader in understanding the application of high-energy electron irradiation to the treatment of toxic and hazardous organic wastes in natural waters.

The literature relating to radiation chemistry most often reports experiments conducted in pure water. The extrapolation of pure water data to natural waters is complicated by the presence of inorganic and organic (primarily humic substances) matter found in natural waters. These compounds may interact with the reactive species formed during irradiation and lead to side reactions not observed in pure water. Examples of these processes are the reactions of hydroxyl radical with carbonate and halide ions.

Irradiation of pure water with fast electrons has been studied extensively with numerous excellent reviews on the subject (1-3). The fast electrons can be generated either by ⁶⁰Co or by electron accelerators. It is thought that the initial radiation process (10⁻¹⁶-10⁻¹⁴ sec) results in the formation of excited molecules H₂O*, H₂O⁺, and e⁻ (4). As these excited state molecules and electrons interact and transfer their energy, several secondary reactive species are formed:



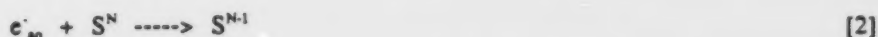
The efficiency of the conversion of energy from ionizing radiation to chemical energy is described by G values. G is defined as the number of radicals, excited states or other products, formed (or lost) in a system absorbing 100 eV of energy. The G value for the formation of the secondary products of irradiation are indicated in parenthesis in equation [1].

Table 1. 25 Most Frequently Identified Substances At 546 Superfund Sites
 (Adapted from McCoy & Assoc., "Haz. Waste. Consult." 3:2(1985))

Rank	Substance	Percent of sites
1	Trichloroethylene	33
2	Lead and compounds	30
3	Toluene	28
4	Benzene	26
5	Polychlorinated biphenyls (PCBs)	22
6	Chloroform	20
7	Tetrachloroethylene	16
8	Phenol	15
9	Arsenic and compounds	15
10	Cadmium and compounds	15
11	Chromium and compounds	15
12	1,1,1-Trichloroethane	14
13	Zinc and compounds	14
14	Ethylbenzene	13
15	Xylene	13
16	Methylene chloride	12
17	<i>trans</i> -1,2-Dichloroethylene	11
18	Mercury	10
19	Copper and compounds	9
20	Cyanides (soluble salts)	8
21	Vinyl chloride	8
22	1,2-Dichloroethane	8
23	Chlorobenzene	8
24	1,1-Dichloroethane	8
25	Carbon tetrachloride	8

The three radicals formed are the most reactive species. The e_{aq}^- and $H^\cdot$ are reducing radicals and the $OH^\cdot$ is an oxidizing radical (5-8). Of these, the aqueous electron and hydroxyl radical account for greater than 90 % of the reactive species. Thus, the chemistry of primary interest in this process is that of these two species. However it is possible that the presences of H_2O_2 may also contribute to the removal of organic toxic and hazardous wastes.

Aqueous Electron. The reactions of the aqueous electron, e_{aq}^- with specific organic and inorganic compounds has been studied extensively (4,5,6,9). The e_{aq}^- is a powerful reducing reagent with an E° ($e_{aq}^- + H \rightarrow \frac{1}{2}H_2$) of 2.77. The reactions of the e_{aq}^- are single electron transfer, the general form of which is:



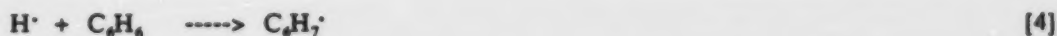
The e_{aq}^- reacts with numerous organic chemicals and of particular interest to the field of toxic and hazardous wastes are the reactions with halogenated compounds. A generalized reaction is shown below:



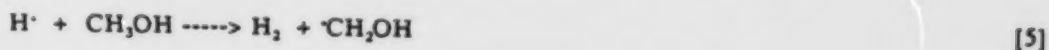
Thus, reactions involving the e_{aq}^- may result in the dechlorination of organohalogen compounds. Further reaction of the organic radical formed could result in the complete destruction of the compound and specific examples are given below. The e_{aq}^- also reacts with other organic compounds and would contribute to the removal of these compounds from aqueous solutions. Examples of the rate constants of reactions of interest in this area are presented later in this paper.

Hydrogen Radical. The reactions of $H^\cdot$ with organic and inorganic compounds have also been summarized (10). The hydrogen atom accounts for approximately 10 % of the total radical concentration in irradiated water. The $H^\cdot$ undergoes two general types of reactions with organic compounds, hydrogen addition and hydrogen abstraction.

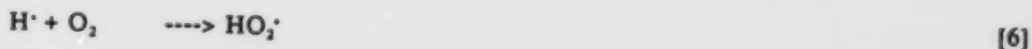
An example of a typical addition reaction with an organic solute is that of benzene:



The second general reaction involving the $H^\cdot$ is hydrogen abstraction:



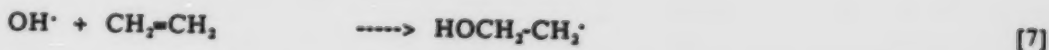
Since most natural waters likely to be encountered will be oxygenated, the predominate reaction will be:



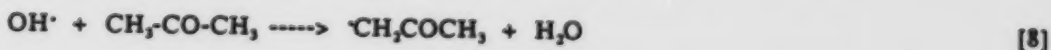
Therefore, it is assumed that the $H^\cdot$ is of minimal importance in the removal of toxic and hazardous organic compounds from oxygenated aqueous solutions.

Hydroxyl Radical. Reactions of the hydroxyl radical, $OH^\cdot$, with inorganic and organic compounds has been well documented (6). Compilations of rate constants have been published (7,10). $OH^\cdot$ can undergo several types of reactions with chemicals in aqueous solution. The types of reactions that are likely to occur are addition, hydrogen abstraction, electron transfer, and radical-radical recombination.

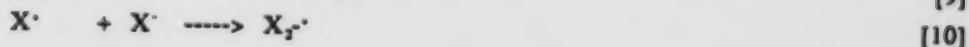
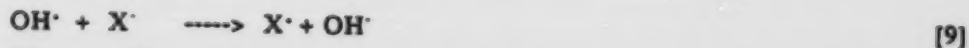
Addition reactions occur readily with aromatic and unsaturated aliphatic compounds. The resulting compounds are hydroxylated radicals:



Hydrogen abstraction occurs with saturated and many unsaturated molecules, e.g., aldehydes and ketones:



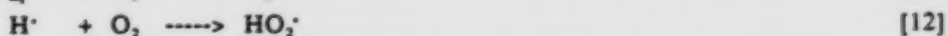
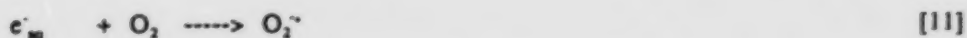
Inorganic electron transfer reactions are also common, and will occur when aqueous solutions are irradiated with high-energy electrons. Reactions involving halogen ions ($X^\cdot$) may also be significant:



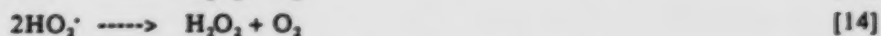
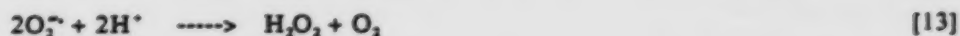
The $X_2^\cdot$ can further react with organic molecules possibly forming halogenated organic compounds. The halogens of most interest are $Cl^\cdot$ and $Br^\cdot$.

Another inorganic radical likely to be involved is $\text{CO}_3^{\cdot -}$. The importance of the carbonate radical is as yet unknown, but because of its relatively low reactivity it will probably play a relatively unimportant role in the removal of most organic compounds. The presence of high concentrations of CO_3^{2-} may have a positive effect on the effective concentration of e_{aq}^- . That is, by removing $\text{OH}^{\cdot}$ from the solution the effective concentration of e_{aq}^- may be higher (no reaction between e_{aq}^- and $\text{OH}^{\cdot}$). This would result in an increased removal efficiency of compounds which react with e_{aq}^- . Another possibly important inorganic compound is H_2S , with a rate constant of $1.83 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Reactions involving H_2S may lead to the formation of sulfur containing organic compounds.

Hydrogen Peroxide. In oxygenated aqueous solutions the reactions of O_2 with e_{aq}^- and $\text{H}^{\cdot}$ occur and compete for the reactive intermediates formed in equation [1]. Both of these reactions result in the formation of reduced oxygen,



The products of equation 11 and 12 are in equilibrium, with a $\text{pK}_a = 4.5$. These products also lead to the formation of additional H_2O_2 :



One of the interesting reactions that has been studied is the following:



with a second order rate constant of $1.2\text{-}1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. In our study, with the high and continuous radiation dose, it appears possible that H_2O_2 might serve as a secondary source of $\text{OH}^{\cdot}$.

ELECTRON BEAM RESEARCH FACILITY PLANT DESCRIPTION:

The Electron Beam Research Facility is located at the Virginia Key (Central District) Wastewater Treatment Plant. It was originally installed as a substitute technology for heat-treatment disinfection of sludge and was declared operational on September 25, 1984. The actual project construction costs at that time were approximately 1.7 million dollars.

The accelerator is a horizontal 1.5 MeV electron beam, rated at 50 Ma. The beam current is continuously variable from 0 to 50 mA, providing doses of 0 - 850 krad.

The research facility was designed to treat 460 liters per minute (120 gallons per minute, gpm), however, experiments have been conducted using flows of up to 610 liters per minute (160 gpm). The minimum flow is approximately 380 liters per minute (100 gpm). Originally designed to disinfect digested sludge, 2-8% solids, the present configuration allows for several influent streams. The influent streams directly connected to the plant are potable (drinking) water, a secondary wastewater effluent and anaerobically digested sewage sludge. The secondary wastewater is the effluent of an extended (pure oxygen) aeration process. The effluent is chlorinated immediately (0.5 - 1 min.) prior to the intake of the electron beam. The sludge contains 2-3% solids.

In addition to the three flow streams described above, we have the capacity to conduct large-scale (22,400 L, 6000 gal.) batch experiments using tank trucks. Batch experiments may be used for groundwater and any other source of contaminated water for which treatability studies are desired. The minimum batch experiment is 7,600 liters (2000 gal).

The electron beam (E-Beam) research facility has been instrumented to continuously monitor and record various operating parameters (accelerating voltage, beam current, water flow) and absorbed dose. The absorbed dose is measured using five resistance temperature devices (RTDs). The five RTDs are mounted in the influent (2 sensors) and effluent (3 sensors) stream immediately before and after the beam. All of the variables are connected via an interface board (Strawberry, Inc.) to a portable computer (Compaq, Inc.) which continuously reads and records temperatures.

ABSORBED DOSE MEASUREMENTS AND PROCESS EFFICIENCY:

Absorbed Dose. Absorbed dose is a measure of energy transfer to the irradiated material, in this case water, and capable of producing chemical or physical changes. In a continuously flowing aqueous system, the absorbed dose can be estimated by measuring the temperature difference of the water stream before and after irradiation. The relationship is derived for pure water by the following:

$$1 \text{ rad} = 100 \text{ erg g}^{-1} \quad [16]$$

or

$$1 \text{ Mrad} = 1.0 \times 10^8 \text{ erg g}^{-1} \quad [17]$$

substituting in,

$$1 \text{ erg} = 2.39 \times 10^{-4} \text{ cal} \quad [18]$$

then

$$1 \text{ Mrad} = 2.39 \text{ cal g}^{-1} \quad [19]$$

converting to °C

$$1 \text{ Mrad} = 2.39 \text{ °C} \quad [20]$$

or,

$$d(t) = 418 \text{ krads °C}^{-1} \quad [21]$$

Thus, the average absorbed dose (D_{AV}) in pure water is calculated using the equation:

$$D_{AV} = K(t_2 - t_1) \quad [22]$$

where, t_1 and t_2 are the before and after irradiation water temperature of the flowing stream in °C, respectively; and K is the constant of proportionality:

$$K = 418 \text{ krads °C}^{-1} \quad [23]$$

Therefore, an increase 1°C in water temperature is equivalent to a dose of 418 krads in pure water.

The measurement of $d(t)$ provides an estimate of absorbed dose in natural waters. A slight error results from the deviation from unit density (pure water) of the natural waters. The application of temperature difference to estimate the absorbed dose in irradiated sludges would result in an error which would increase with increasing solids content.

Concentration of Reactive Species. It is possible, using the estimate of absorbed dose and G values, to determine the approximate concentration of the species in equation [1]. Substituting the following:

$$1 \text{ erg} = 6.24 \times 10^5 \text{ MeV} = 6.24 \times 10^{11} \text{ eV} \quad [24]$$

it follows from equation [15] that:

$$1 \text{ rad} = 6.24 \times 10^{13} \text{ eV g}^{-1} \quad [25]$$

and,

$$1 \text{ Mrad} = 6.24 \times 10^{19} \text{ eV g}^{-1} \quad [26]$$

$$= 6.24 \times 10^{22} \text{ eV L}^{-1} \text{ of H}_2\text{O} \quad [27]$$

For a chemical with a G = 1,

$$1 \text{ Mrad} = 6.24 \times 10^{22} \text{ eV L}^{-1} / 100 \text{ eV molecule}^{-1} \quad [28]$$

$$= 6.24 \times 10^{20} \text{ molecules L}^{-1} \text{ of H}_2\text{O} \quad [29]$$

dividing by Avogadro's number ($N_A = 6.02 \times 10^{23} \text{ molecules mole}^{-1}$), the result is,

$$1 \text{ Mrad} = 1.04 \times 10^{-3} \text{ mole L}^{-1} = 1.04 \text{ mM} \quad [30]$$

Thus, for a G value of 2.7, e.g., $\text{OH}^\cdot$ from equation 1, and an absorbed dose of 1 Mrad, there are 2.81 mmol of $\text{OH}^\cdot$ formed.

Apparent G Value. Considerable research has lead to G values for the formation of the secondary products of fast electron irradiation of pure water. To apply the concept of G values to the disappearance of organic compounds at low concentrations and natural waters, an absolute number is not possible at this time. The loss or removal of an organic compound in irradiated solutions depends on several factors, e.g., dose rate, the quality (purity) of the natural water, the concentration of organic solute, and the presence of other radical scavengers in the solution being studied. To account for the uncertainty encountered in these solutions, an apparent G value, G_{app} is used. G_{app} is defined by assuming a G = 1 for the formation of all reactive species in an irradiated solution. Then from equation [30] above, the total concentration of reactive species formed in a solution that receives 1 Mrad absorbed dose is 1.04 mM. The G_{app} is determined by solving the following equation:

$$G_{\text{app}} = \text{OS}_d / \text{RS}_d \quad [31]$$

where, OS_d = the change in concentration of the organic solute at a given dose, d; and,

RS_d = the concentration of reactive species, assuming a G value of 1, at the absorbed dose, d.

The absorbed dose is determined by the temperature difference method outlined above. For example, at a dose of 200 krads, $3.07 \times 10^{-4} \text{ M}$ of a compound is removed from solution as a

result of the irradiation process. The concentration of the reactive species at 200 krad is 2.08×10^{-4} M. Then,

$$\begin{aligned} G_{app} &= 3.07 \times 10^{-4} \text{ M} / 2.08 \times 10^{-4} \text{ M} \\ &= 1.48 \times 10^{-2} \end{aligned} \quad [32]$$

The value of G_{app} is determined from the disappearance of organic chemicals in aqueous solutions. One focus of the research being conducted by our group is a comparison of G_{app} determined by ^{60}Co , gamma irradiation, and that obtained using high-energy electron irradiation. If the trends observed to date hold, it will be possible to predict the removal of organic compounds in natural waters at the Electron Beam Research Facility, based upon laboratory data obtained in similar water.

ELECTRON UTILIZATION EFFICIENCY:

It is possible to estimate the electron utilization efficiency of the system at the Electron Beam Research Facility, described above. Assuming that the system is operated at full power, i.e. 1.5 MeV and 50 Ma, total beam power of 75 kW, and at a flow rate of 120 gal min^{-1} , or $2.73 \times 10^7 \text{ mL hr}^{-1}$, then the efficiency may be determined as follows:

$$1 \text{ W} = 860 \text{ cal hr}^{-1} \quad [33]$$

$$75 \text{ kW} = 6.45 \times 10^7 \text{ cal hr}^{-1} \quad [34]$$

Complete conversion of electrical energy (beam power) to heat would result in a $d(t)$ of, assuming that 1 cal results in a 1°C increase in temperature per gram,

$$\begin{aligned} d(t) &= 6.45 \times 10^7 \text{ cal hr}^{-1} / 2.73 \times 10^7 \text{ mL hr}^{-1} \\ &= 2.36^\circ\text{C} \end{aligned} \quad [35]$$

We observed a 1.54°C increase in temperature (645 krad). Therefore the efficiency of the conversion of beam energy to heat was,

$$\text{efficiency (\%)} = 1.54^\circ\text{C} / 2.36^\circ\text{C} \times 100 = 65.3 \% \quad [36]$$

In limited experiments at high water flow rates, 160 gal min^{-1} or $3.63 \times 10^7 \text{ mL hr}^{-1}$, the dose was unchanged, i.e. 645 krad or 1.54°C increase in temperature, and the efficiency approached 86%. The reasons for the increase in efficiency were probably related to the more complete

absorption of the fast electrons in the solution (increased depth of the water), and, at the higher flow rate the water cascaded over the weir nearer to the electron gun window, reducing energy losses in the air between the window and the water.

REMOVAL OF TOXIC AND HAZARDOUS ORGANIC CHEMICALS IN AQUEOUS SOLUTION:

We have conducted numerous experiments with organic chemicals that may be of interest in: water treatment, trihalomethanes; groundwater contamination, halogenated ethanes and ethenes; leaking underground storage tanks, benzene and substituted benzenes; as well as other organic chemicals now regulated as hazardous wastes. Before presenting removal efficiencies, a brief discussion and summary of the selected rate constants are presented for the compounds that have been studied or that are of interest in the area of toxic and hazardous wastes.

Rate Constants. The rate constants of interest are those for the reaction of the reactive intermediates formed when water is irradiated (equation 1), e_{aq}^- , $H^\cdot$, and $OH^\cdot$, with toxic and hazardous organic chemicals, and inorganic chemicals likely to be found in natural waters. A review of the literature (10) for selected rate constants applicable to toxic and hazardous wastes is summarized in Table 2.

Removal Efficiencies and Possible Reaction Mechanisms. The experiments discussed below have been conducted on a large scale treatment facility, and, although some of the results appear to be qualitatively explained using available rate constants, other results do not fit.

Table 2. Rate Constants ($M^{-1} s^{-1}$) of Selected Organic Chemicals and the Free Radicals Formed in Irradiated Aqueous Solution (10).

Compound	e_{aq}^-	$H^\bullet$	$HO^\bullet$
Benzene	9.0×10^6	9.1×10^8	7.8×10^9
Bromodichloromethane	NF ^{**}	NF	NF
Bromoform	NF	NF	NF
Carbon Tetrachloride	1.6×10^{10}	3.8×10^7	NF
Chlorobenzene	5.0×10^8	1.4×10^9	5.5×10^9
Chloroform	3.0×10^{10}	1.1×10^7	5×10^6
<i>o</i> -Cresol	NF	NF	1.1×10^{10}
<i>m</i> -Cresol	NF	NF	NF
<i>p</i> -Cresol	4.2×10^7	NF	1.2×10^{10}
Dibromochloromethane	NF	NF	NF
1,2-Dichlorobenzene	4.7×10^9	NF	NF
1,3-Dichlorobenzene	5.2×10^9	NF	NF
1,4-Dichlorobenzene	5.0×10^9	NF	NF
1,1-Dichloroethane	NF	NF	NF
1,2-Dichloroethane	NF	NF	NF
1,1-Dichloroethylene	NF	NF	NF
<i>trans</i> -1,2-Dichloroethylene	7.5×10^9	NF	6.2×10^9
2,4-Dinitrotoluene	NF	NF	NF
Ethylbenzene	NF	NF	7.5×10^9
Hexachlorobenzene	NF	NF	NF
Hexachloro-1,3-butadiene	NF	NF	NF
Hexachloroethane	NF	NF	NF
Methylene Chloride	NF	NF	NF
Methyl ethyl ketone	NF	NF	NF
Nitrobenzene	3.7×10^{10}	1.0×10^9	3.9×10^9
Pentachlorophenol	NF	NF	NF
Phenol	2.0×10^7	1.7×10^9	6.6×10^9
Pyridine	1.0×10^9	7.8×10^8	3.1×10^9
Tetrachloroethylene	1.3×10^{10}	NF	2.8×10^9
Toluene	1.4×10^7	2.6×10^9	3.0×10^9
1,1,1-Trichloroethane	NF	NF	NF
Trichloroethylene	1.9×10^9	NF	4.0×10^9
2,4,5-Trichlorophenol	NF	NF	NF
2,4,6-Trichlorophenol	NF	NF	NF
Vinyl Chloride	2.5×10^8	NF	1.2×10^{10}
<i>m</i> -Xylene	NF	2.6×10^9	7.5×10^9
<i>o</i> -Xylene	NF	2.0×10^9	6.7×10^9
<i>p</i> -Xylene	NF	3.2×10^9	7.0×10^9

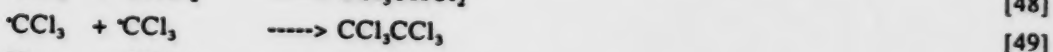
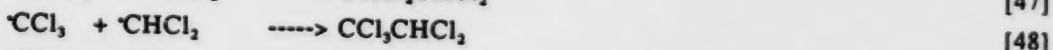
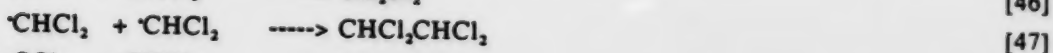
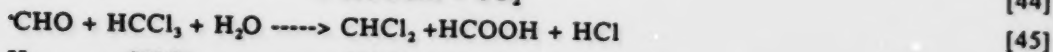
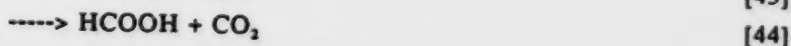
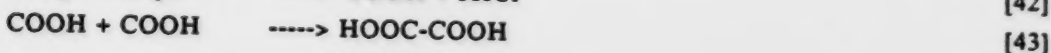
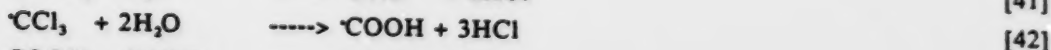
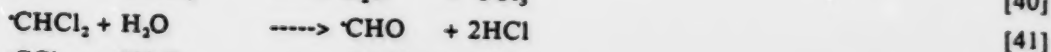
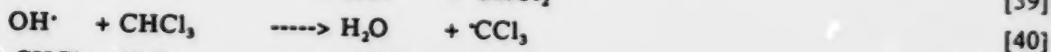
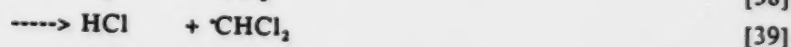
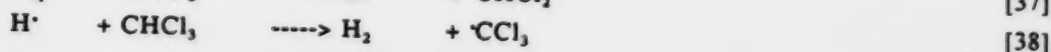
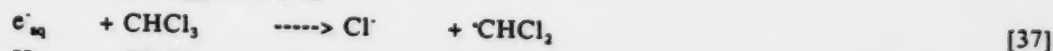
* many experiments conducted at low pH

** not found.

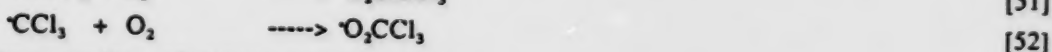
These differences are not surprising given that the rate data reported in the literature are usually obtained in pure solutions under controlled experimental conditions. Thus, there may be several reasons for the apparent discrepancies. First, all of the experiments have been conducted in raw or secondary treated wastewater or potable water. These waters are of widely varying (water) quality and present a complex matrix for detailed examination of removal data. Secondly, not all of the applicable rate constants are known for the compounds of interest.

One of the initial chemical groups studied at our facility was the halogenated methanes. Others have reported studies using electron and gamma irradiation of aqueous solutions of chloroform (11,12). We have studied CHCl_3 and CHBr_3 and observed removal efficiencies of CHCl_3 of approximately 85 - 99.9% in secondary and raw wastewater, and potable water, respectively. Figure 1 shows typical removal profiles for CHCl_3 in both potable water and raw wastewater. Figure 2 shows the removal efficiency of CHBr_3 in raw wastewater and potable water. The removal efficiency of CHBr_3 is apparently not affected by the change in water quality and is independent of concentration in the range of 100 - 1500 $\mu\text{g L}^{-1}$.

A proposed mechanism for the decomposition of CHCl_3 and the formation of reaction by-products has been suggested (12):



and in solutions with high O_2 concentrations the following reactions are also possible:



with the exact fate of these radicals unknown.

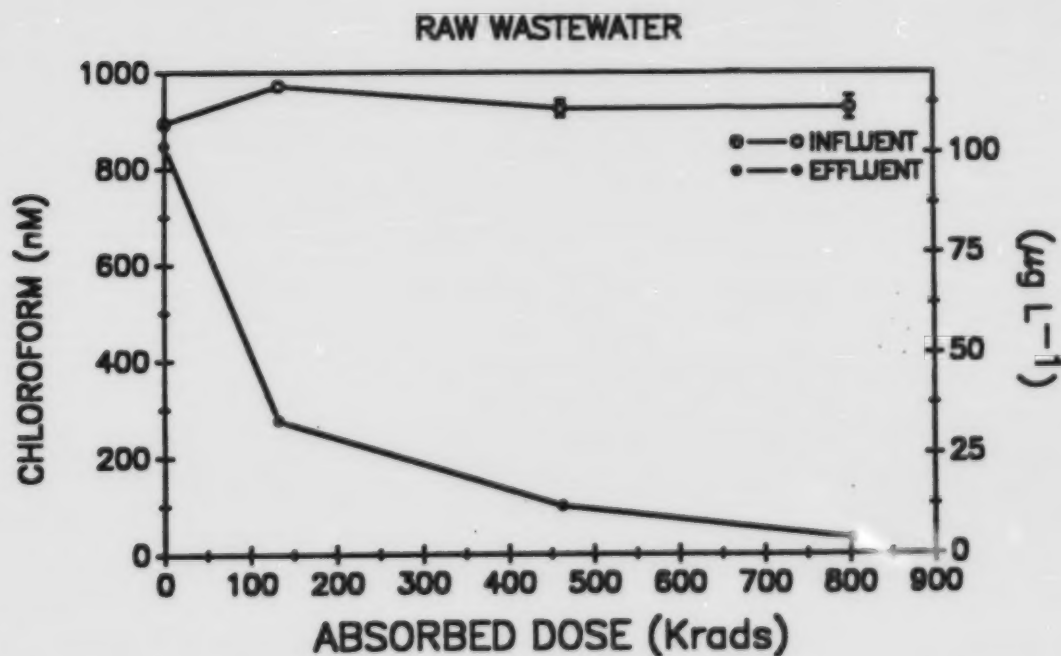
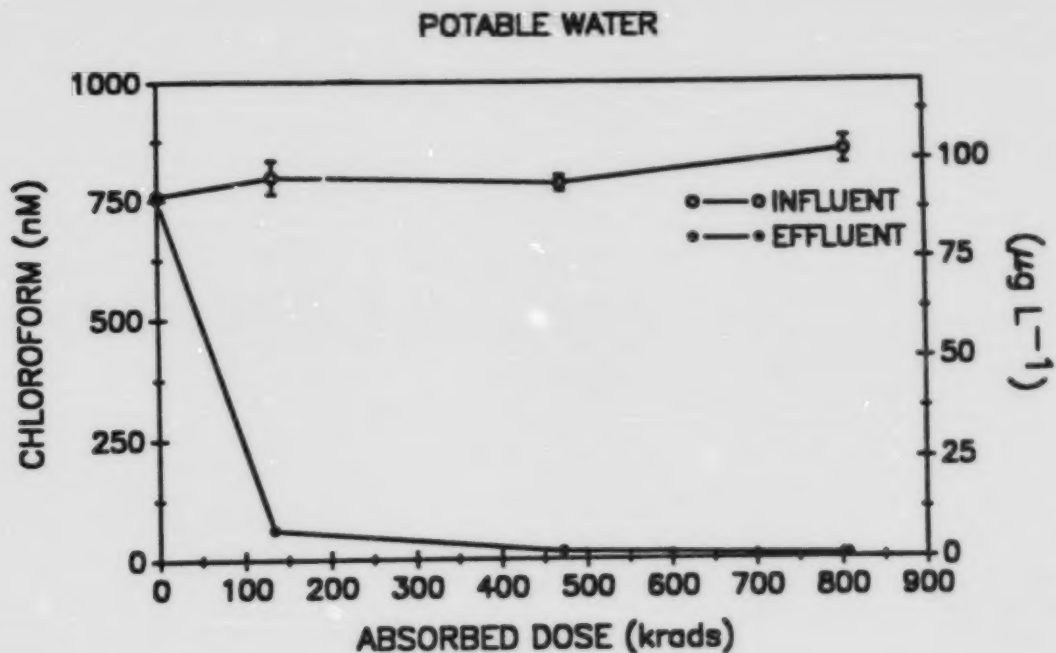


Figure 1. Removal of CHCl_3 at several irradiation doses in both potable water and raw wastewater (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

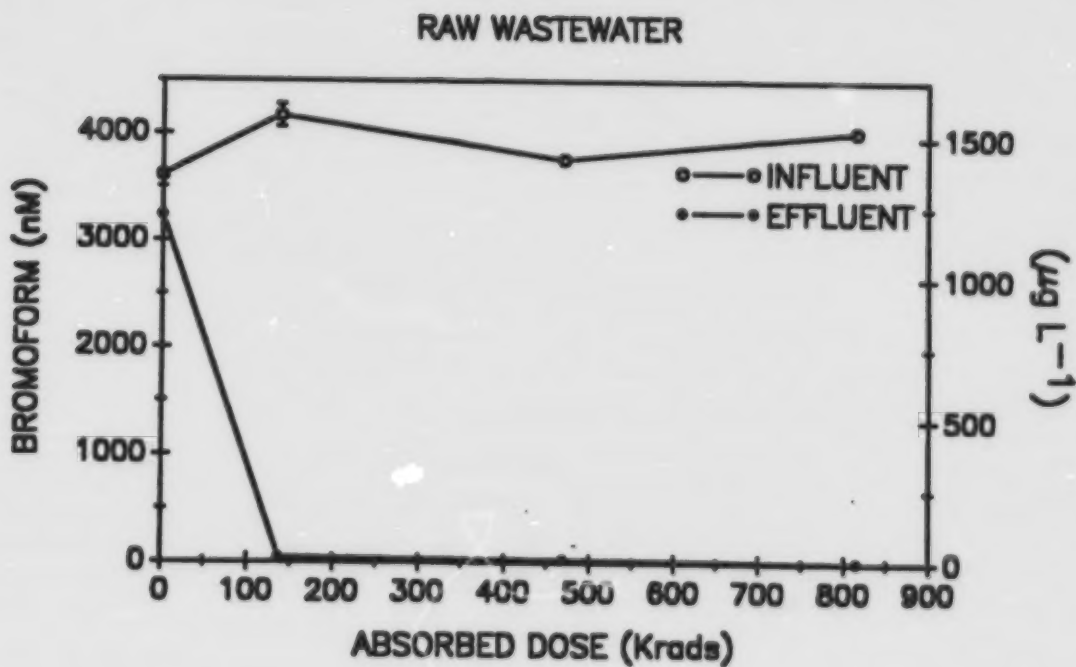
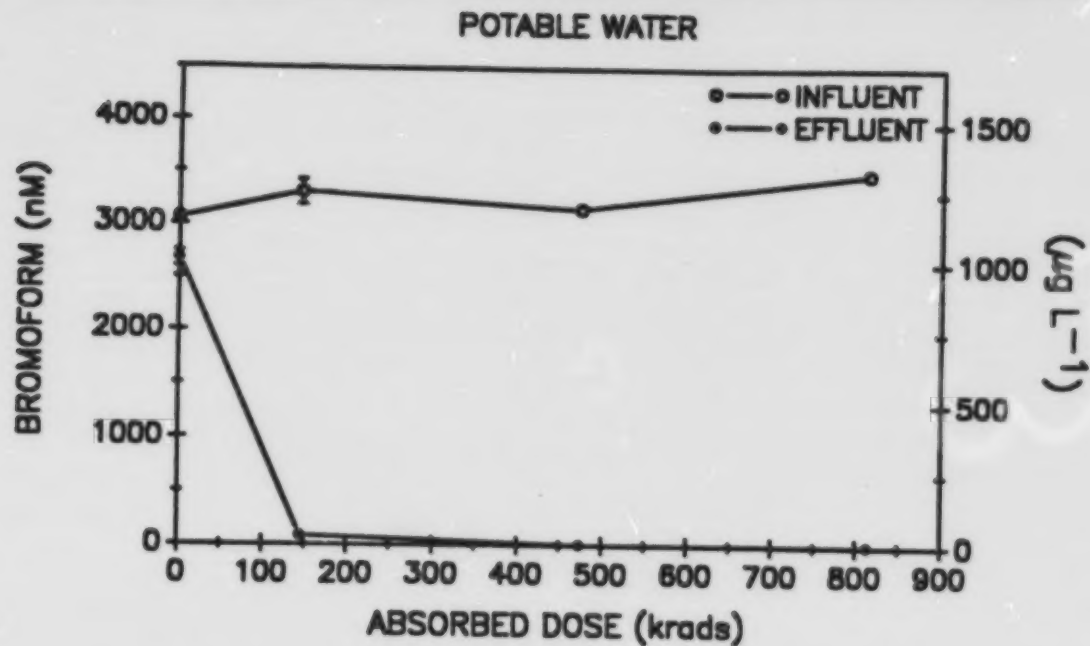


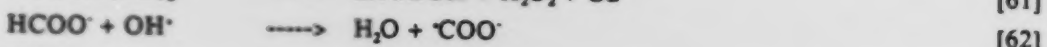
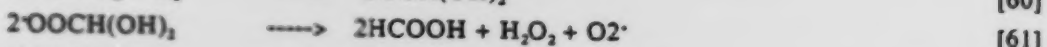
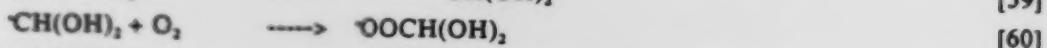
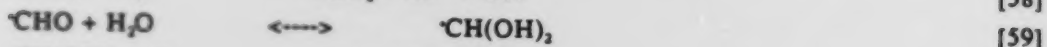
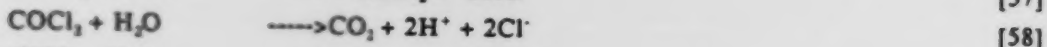
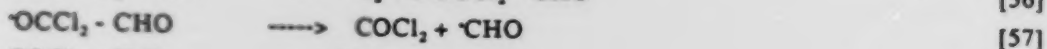
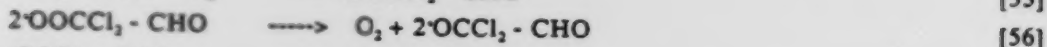
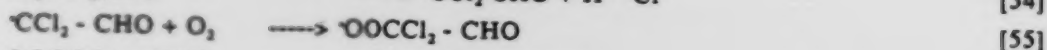
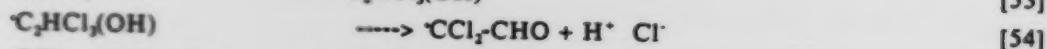
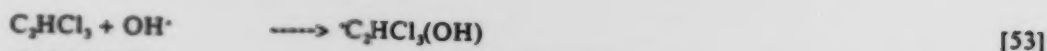
Figure 2. Removal of CHBr₃ at several irradiation doses in both potable water and raw wastewater (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

The major differences between the work which resulted in the above reaction mechanism (12) and our work are 1) the concentration of the CHCl_3 was 70 mM, whereas the concentration range we have been studying is 1000 fold less, and 2) the irradiation doses we use are up to 100 fold higher. In our studies, conducted at low solute concentrations, none of the halogenated reaction by-products have been observed. The liquid-liquid extraction method used for the quantification of the CHCl_3 , would also have determined the presence of the chlorinated ethanes at detection limits of $0.01 \mu\text{L}$. The authors (12) found that the presence of O_2 enhanced the decomposition of the CHCl_3 . This is of importance because many of the systems in which this process will be potentially used involve solutions which will have been aerated or at least contain some O_2 .

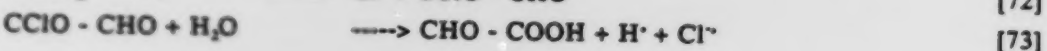
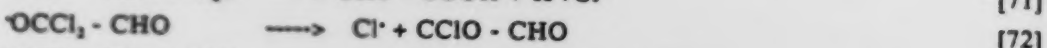
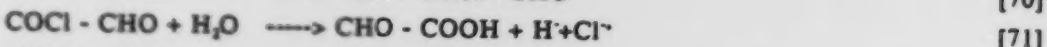
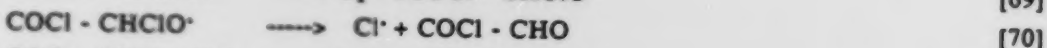
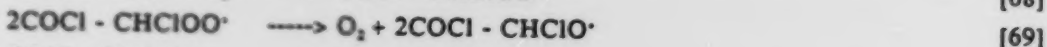
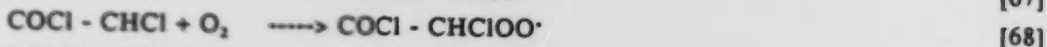
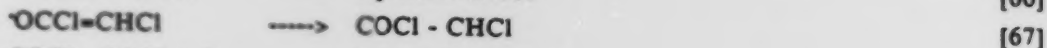
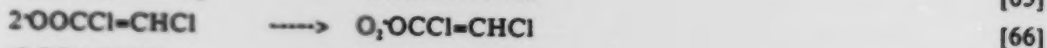
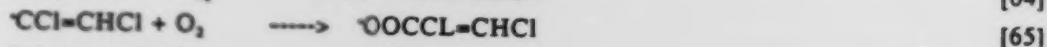
Whether the above mechanism describes the actual breakdown process in natural waters will never be known quantitatively. The importance of the above mechanism (equations 37 - 52) is that it provides a point of departure for determining other possible reaction products. We have observed, in preliminary research, that oxidized organic compounds, such as formaldehyde, are formed. Continuing research is underway using analytical methods for the determination of very low concentrations of aldehydes and carboxylic acids.

Another group of organic chemicals that have been studied at our treatment facility are the halogenated solvents. The compounds of most note are trichloroethylene (TCE) and tetrachloroethylene (PCE). Radiation induced decomposition of TCE in aqueous solutions has been the subject of several recent studies (13-18). An example of the removal efficiency we have obtained in secondary wastewater is shown in Figure 3. In most of the referenced studies conducted to date the complete destruction of TCE was observed. Although the preliminary data indicated a relationship between removal efficiency and second order reaction rate constants of $\text{OH}^\bullet$, it is also possible that the e_{aq}^- may be in part responsible for the removal of TCE.

A proposed mechanism for the destruction of TCE by OH⁻ is as follows:



and TCE and e_{aq}^- :



SECONDARY WASTEWATER

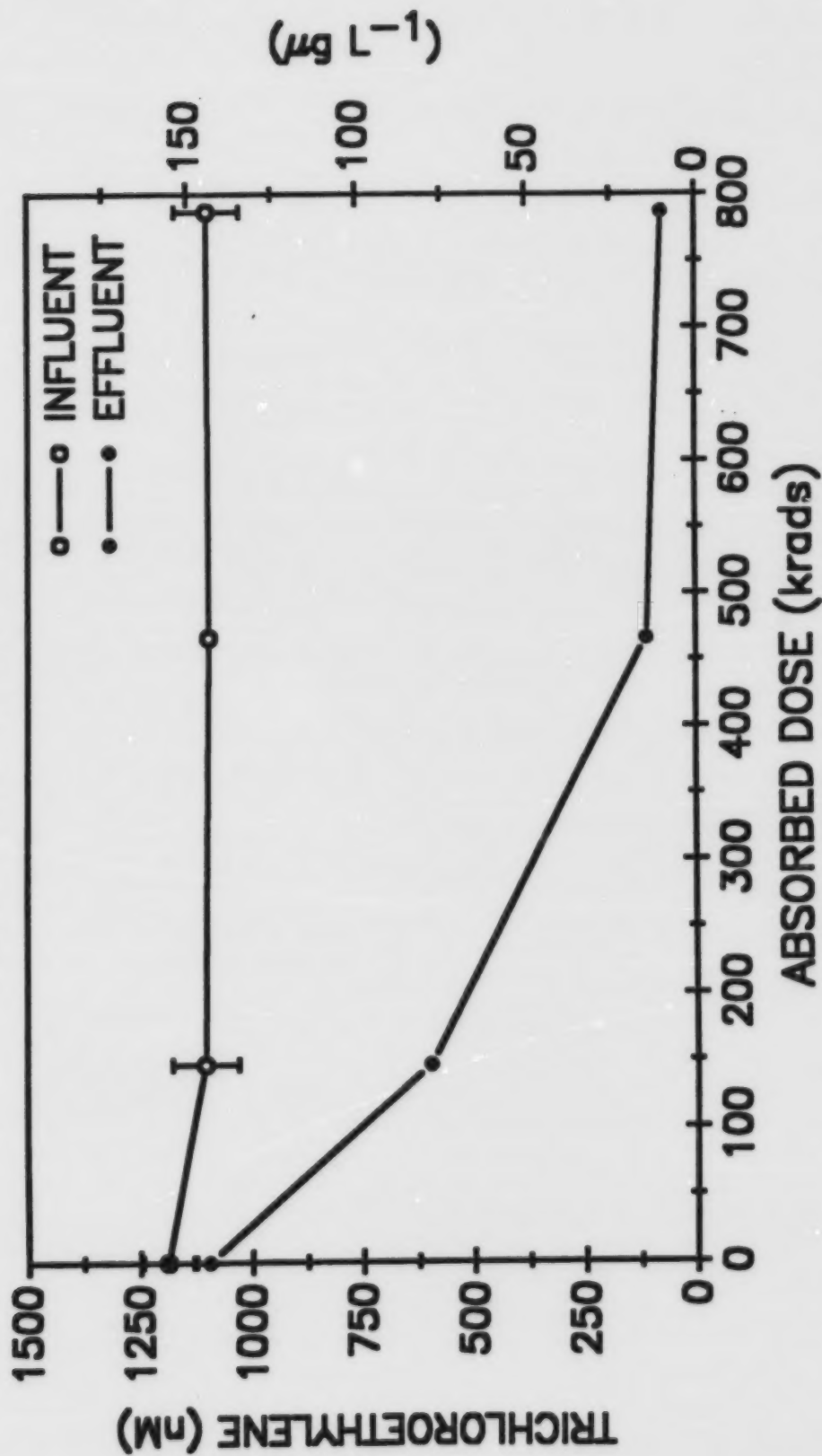


Figure 3. Removal of TCE at several irradiation doses in oxygenated secondary effluent (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

The major stable reaction products for the irradiation of TCE in aqueous solution are oxidized polar organic compounds. Studies are underway to identify the reaction by-products in natural water irradiated with high-energy electrons.

Considerable research has also been reported on the irradiation of aqueous solutions of PCE (13-16,18-21). As with TCE, it appears that complete destruction occurs as evidenced by chloride ion mass balance. This observation, insofar as loss of the parent compound PCE, has been confirmed in our studies in secondary wastewater at low concentrations, with the higher initial concentrations resulting in > 95% removal (Figure 4).

A third group of compounds which we have studied are benzene and substituted benzenes. Numerous studies have been reported on the effect of irradiation of aqueous solutions of benzene (22-29). We have also shown that benzene is very effectively removed from an oxygenated secondary wastewater effluent (Figure 5). From the studies reported in the literature, it is possible to propose mechanisms for the destruction of benzene. The principal reaction products expected at low doses are phenols and at high doses are highly oxidized aliphatic aldehydes and carboxylic acids. However, it is possible that biphenyl and hydroxybiphenyl might also be formed. We were able to identify formaldehyde and glyoxal in sub- μ M concentrations in several samples. Several other aldehydes were observed but the structures of these reaction products has not yet been determined.

The irradiation of toluene has also been studied in aqueous solution (30). In preliminary experiments using an oxygenated wastewater effluent, we observed removal efficiencies approaching 97% as shown in Figure 6.

Initially irradiation of aqueous solutions of either benzene (see below) or toluene will result in the intermediate formation of phenols. Figure 7 shows that as the irradiation dose increases, the phenols increase then decrease to concentrations below influent concentrations. Additional preliminary results suggested that the addition of H_2O_2 at low concentrations might enhance the removal of aromatic compounds. This suggests that the addition of H_2O_2 might be a possible way in which to improve the overall efficiency of the process.

SECONDARY WASTEWATER

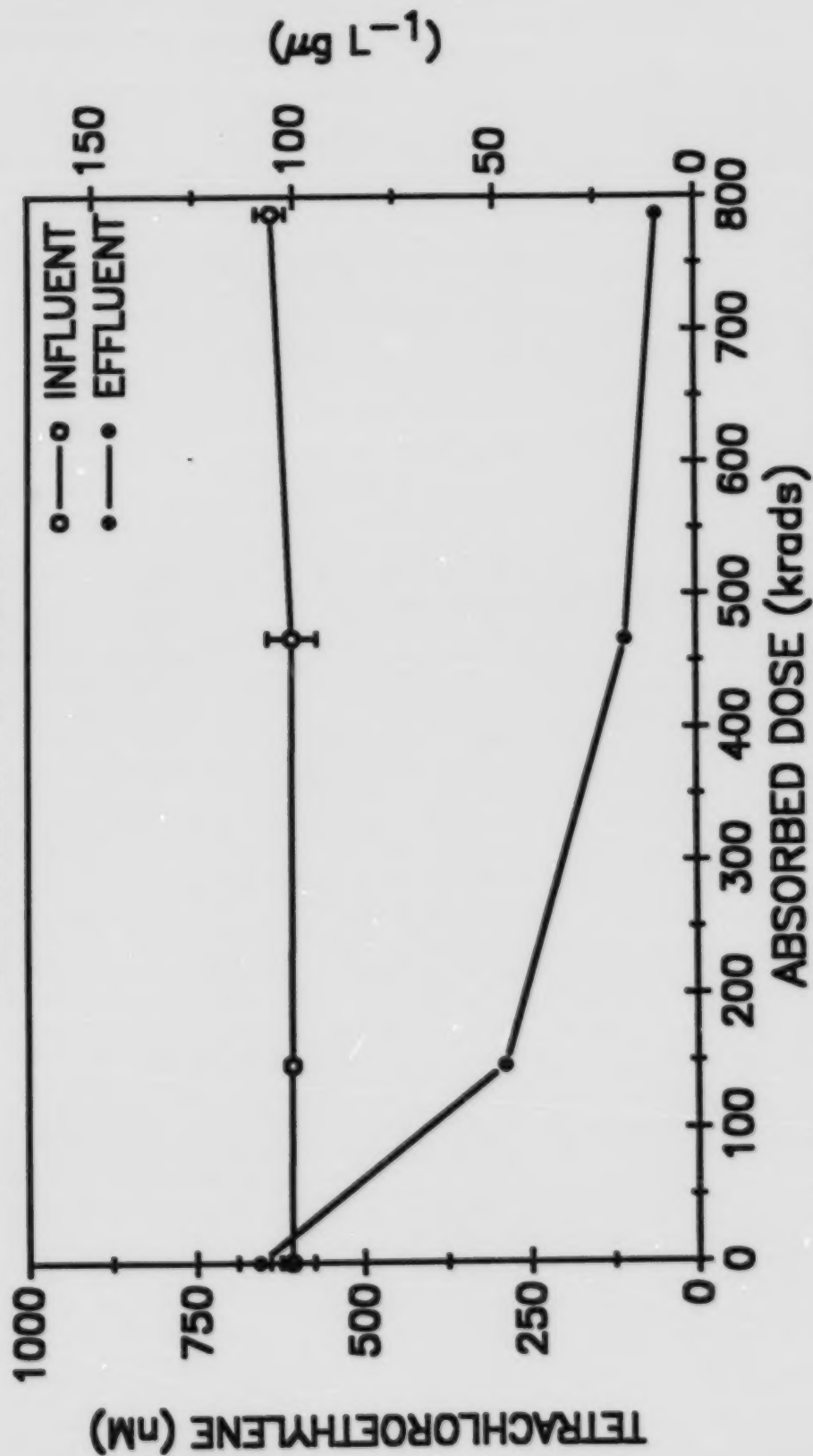


Figure 4. Removal of PCE at several irradiation doses in oxygenated secondary effluent (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

SECONDARY WASTEWATER

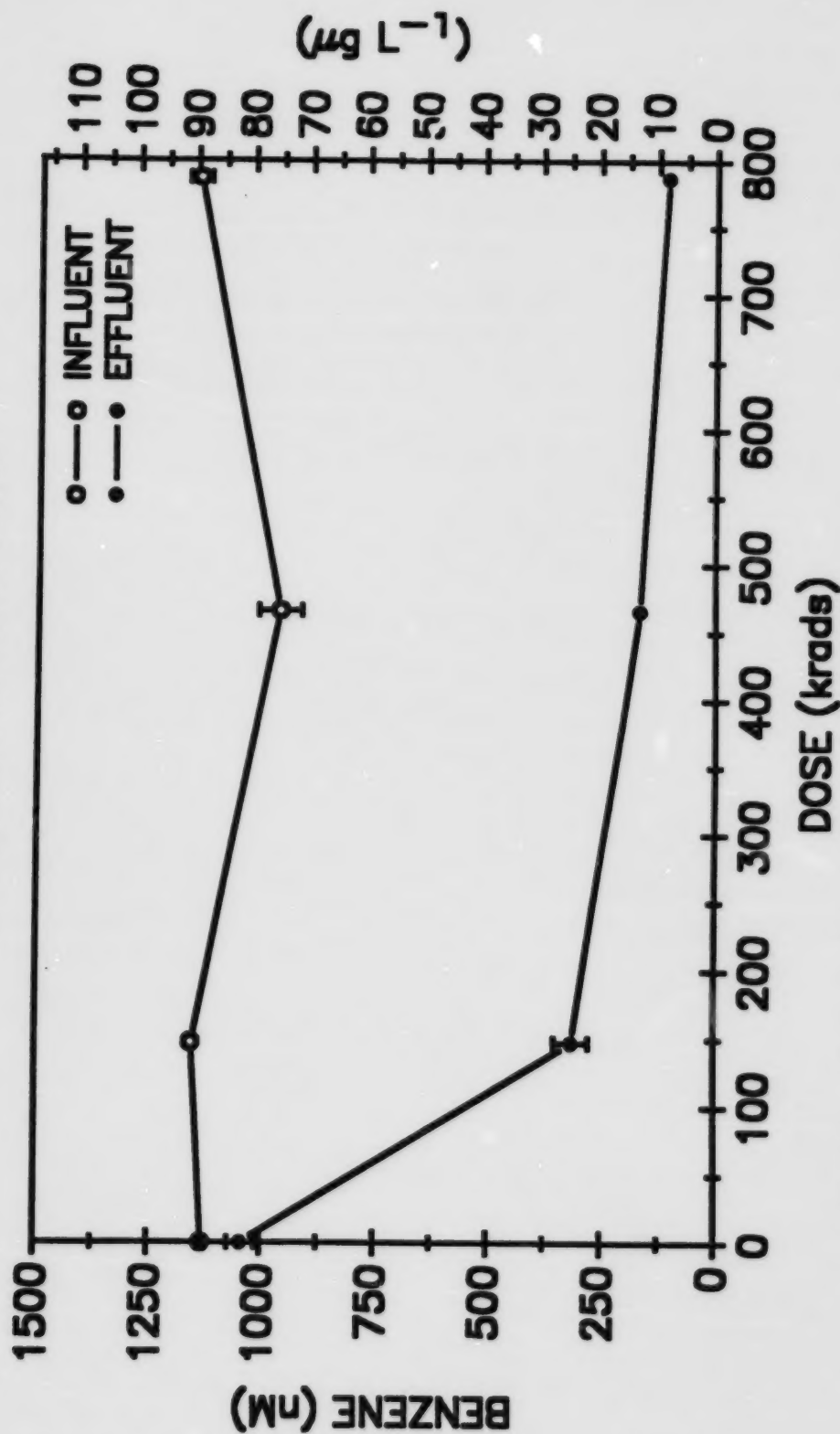


Figure 5. Removal of Benzene at several irradiation doses in oxygenated secondary effluent (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

SECONDARY WASTEWATER

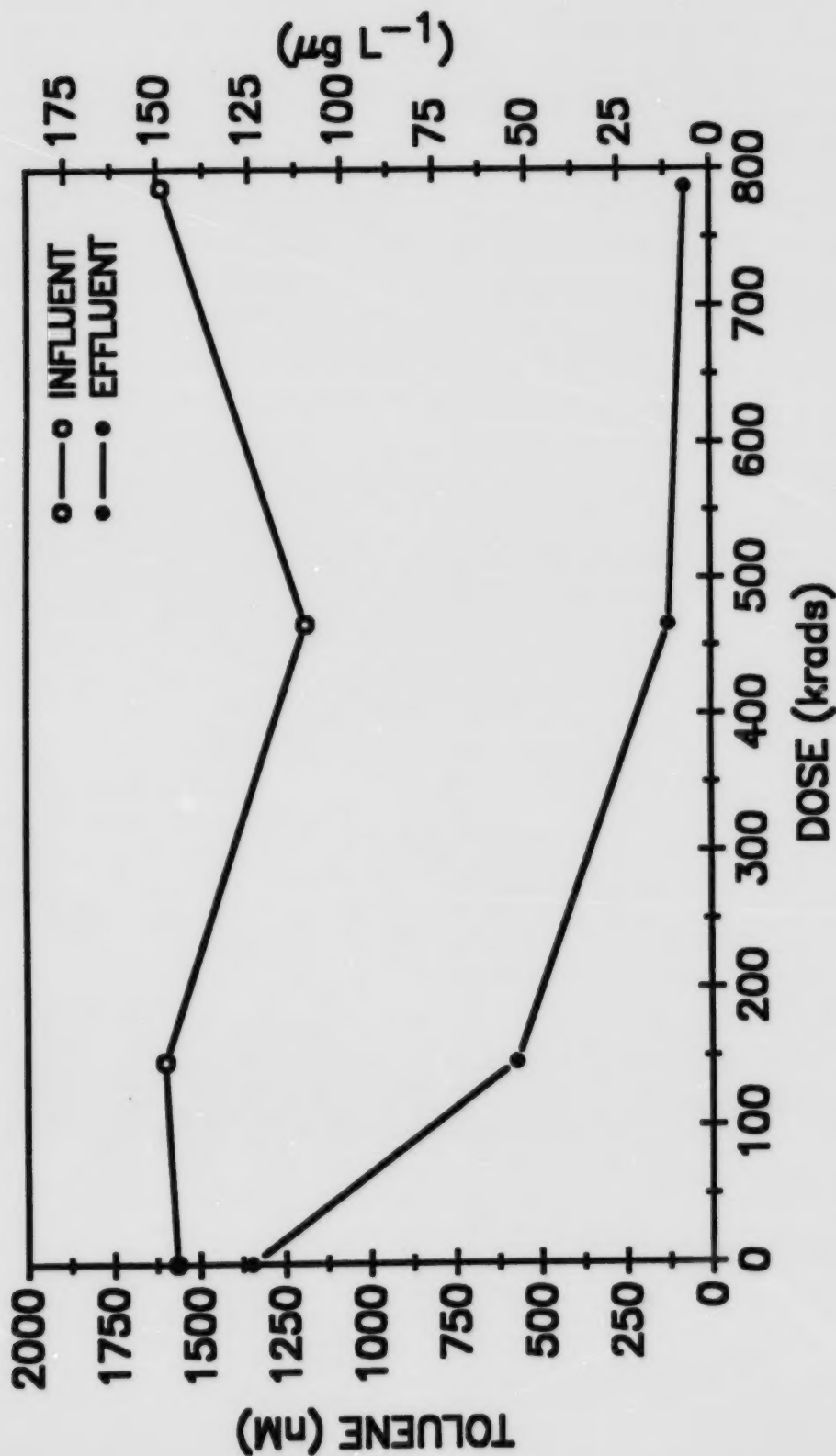


Figure 6. Removal of Toluene at several irradiation doses in oxygenated secondary effluent (error bars indicate one standard deviation from mean, where no error bars are seen the error is within the data point).

Irradiation of phenol has been shown in preliminary research to result in its disappearance (see Figure 7). The irradiation of phenol has also been reported in the literature (31-33). The mechanisms proposed for benzene are applicable to phenol, as it is one of the first reaction products of $\text{OH}^\cdot$ attack on benzene. Thus, the discussion of reaction products above should suffice for phenol as well. We have not conducted any experiments on phenol in which phenol was determined by HPLC.

In summary, we have shown that the use of high-energy electrons can effectively remove organic compounds from waters of varying quality. Although the removal efficiency is somewhat water quality dependent, water quality is less important than when considering other advanced oxidation processes for the removal of toxic organic compounds.

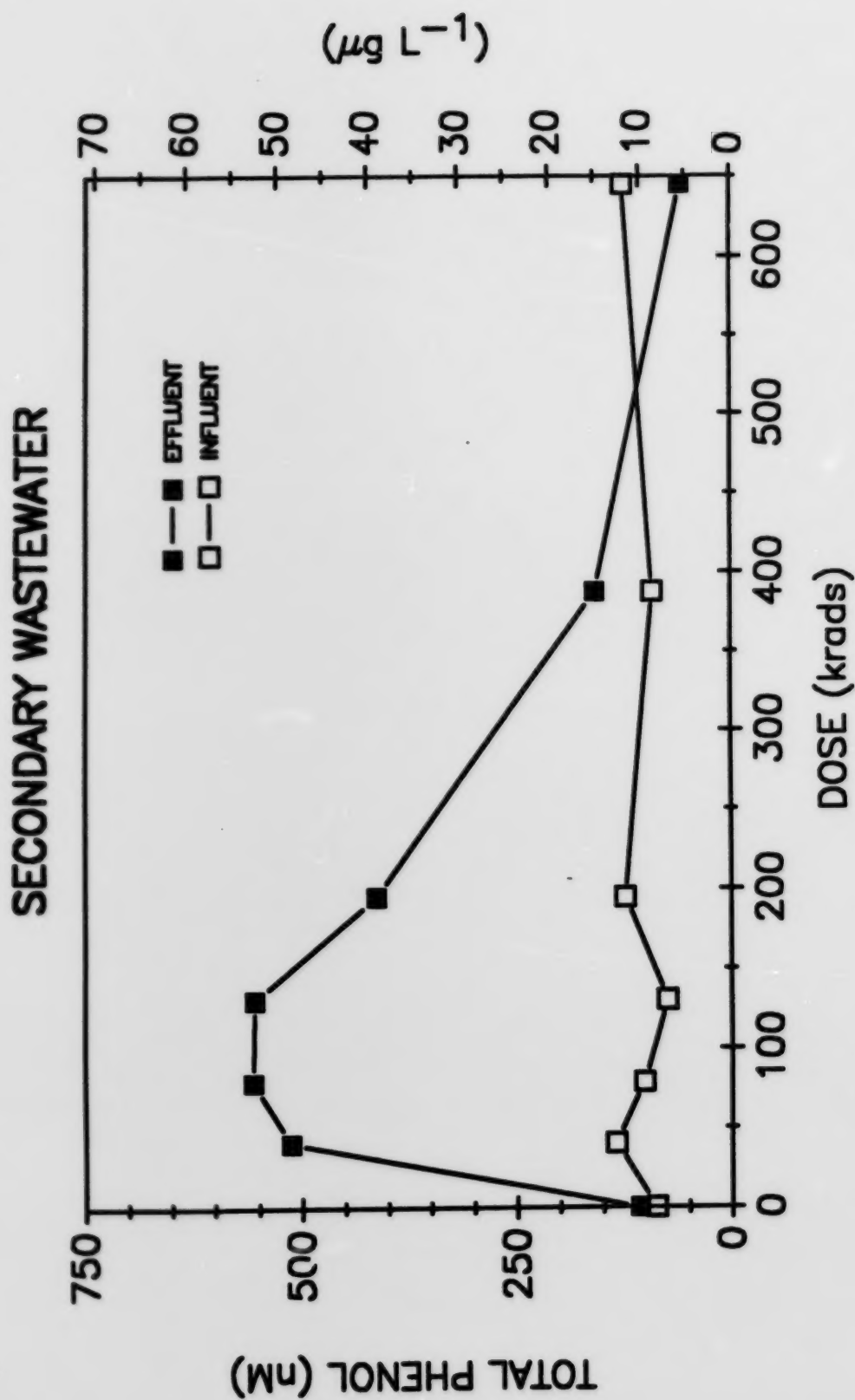


Figure 7. Formation and decomposition of phenol(s) during the irradiation of benzene and substituted benzenes, at several irradiation doses, in oxygenated secondary effluent.

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SOLAR DETOXIFICATION OF WATER

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ABSTRACT:

Current work on the use of concentrated sunlight in the destruction of hazardous organic contaminants in water will be discussed. The characteristics of the terrestrial solar spectrum as a source of near-ultraviolet (UV) radiation will be described as the spectrum relates to the activation of semiconductors in water. The effects of light intensity, pH, initial concentration, and background mineral content of the water on the rate of destruction of trichloroethylene will be described for the titanium dioxide system. Experiments comparing immobilized and suspended TiO_2 were carried out.

INTRODUCTION:

Contamination of groundwater by hazardous organic compounds is a major environmental problem throughout the world. In the United States the Environmental Protection Agency (EPA) has identified compounds that present particular health hazards. These have been published in the Priority Lists of Hazardous Substances Commonly Found at Superfund Sites (1) and the Toxic Chemical Release Inventory (2). There are currently more than 400 organic compounds on these two lists. As part of the Conservation and Renewable Energy Program of the U.S. Department of Energy, work is under way to develop innovative solar processes that can be used to destroy hazardous organic chemicals in water.

Solar detoxification of water is based on a body of work that has been developed in the field of semiconductor photoelectrochemistry over the last two decades. It is well established that a variety of organic compounds can be completely mineralized in water over polycrystalline semiconductors when they are irradiated with light exceeding the band gap of the semiconductor in energy (3,4,5). The anatase form of titanium dioxide has been studied in the most detail and, in general, is found to be the most effective for the process. The active oxidizing agent is believed to be hydroxyl radical which is generated at hole sites in the valence band of the photoexcited semiconductor. About 10% of the compounds in the EPA lists have been demonstrated to be photochemically destroyed in the presence of illuminated

aqueous TiO_2 (6). Most of these have been chlorinated aliphatic, olefinic, or aromatic compounds of the types used as solvents, wood-treating agents, or insecticides. Even a conservative extrapolation of these investigations suggests that more than triple the number of compounds on the EPA lists could probably be treated by this chemistry.

Current work is directed toward the destruction of chlorinated solvents such as trichloro- and perchloro-ethylene (TCE and PCE) because they are widely found in groundwater at levels exceeding the limit set by EPA regulations. We report here results of work on TCE destruction rates in both synthetic solutions and in groundwater samples from a contaminated site. In addition, measurements comparing the output of artificial light sources with the near-UV region of the solar spectrum (300-400 nm) are included because these data are critical to extrapolation of laboratory data to predict the performance of a solar process.

RESULTS:

Experimental procedures have been reported elsewhere (7). Except as otherwise noted, experiments were done using a 1000-W xenon arc lamp; wavelengths below 300 nm and above 450 nm were rejected by a Schott WG-305 filter and a dichroic mirror, respectively. The rates of destruction of TCE were determined as a function of initial concentration, light intensity, pH, and hydrogen peroxide concentration using suspended TiO_2 . The rate of destruction of TCE in contaminated groundwater was determined over suspended TiO_2 . The rate of destruction of TCE over two immobilized forms of TiO_2 was also measured. Destruction rates are adequately represented by a first-order rate expression for each individual case. The dependence of the first-order initial rate constants on the initial concentration of TCE can be modeled by the Langmuir-Hinshelwood equation, which has been widely used to model destruction kinetics in the TiO_2 system (8).

In unbuffered solution, the apparent rates of TCE mineralization are found to increase with decreasing initial concentration, varying from 0.35 min^{-1} at 60 ppm to 3 min^{-1} at 0.3 ppm (Table 1). This behavior agrees with Langmuir-Hinshelwood kinetics which predict that the pseudo first-order rate constant will increase with decreasing initial reactant concentration. Data are also included that compare the rate of destruction of TCE in a sample of contaminated groundwater with that in similar initial concentrations in synthetic mixtures. Under the test conditions the destruction rates were similar. The pH of solutions drops during the mineralization reaction as a result of the formation of HCl. This pH change can influence many of the reactions that are proposed to occur in the $\text{H}_2\text{O}/\text{O}_2/\text{TiO}_2$ system at the semiconductor valence and conduction bands (9). Experiments were done in buffered solution

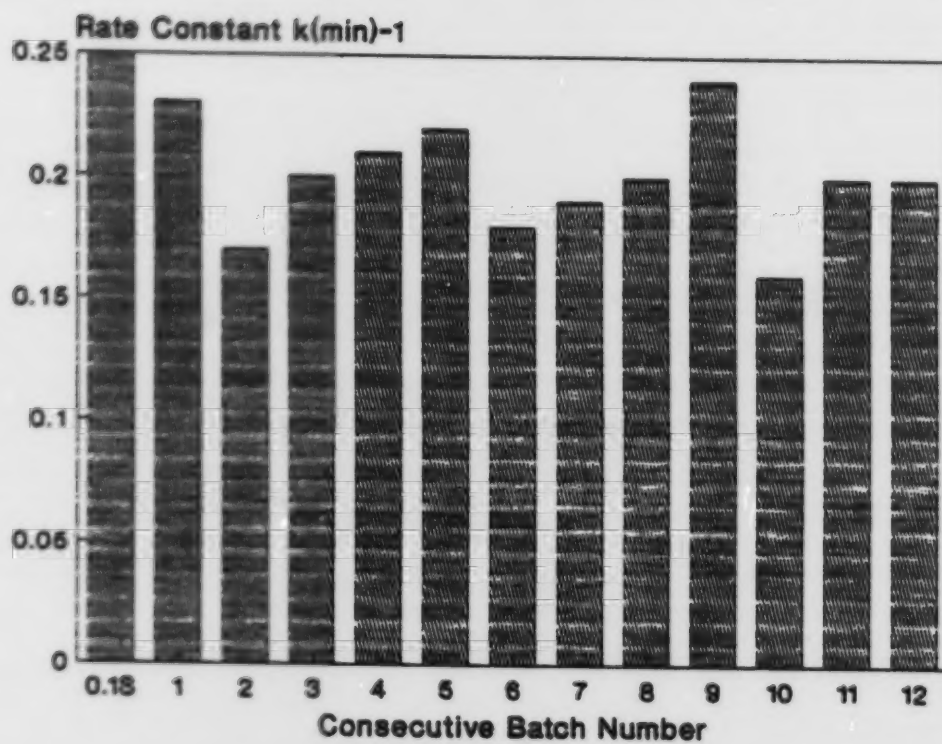


Figure 1. TCE decomposition, thermally dried fixed bed TiO_2

in an attempt to determine the effect of pH on the rate of mineralization. In initial experiments, potassium hydrogen phthalate was used as the buffer. Because the phthalate ion can also be attacked by hydroxyl radical, buffering introduces a species that can be competitive with destruction of TCE. Consequently, although the results in Table 2 may be indicative of a pH effect on rate, they must be interpreted cautiously.

For solar processes, concentration of the sunlight presents some advantages in the design of systems. Information in the literature suggests that at low light intensities the rate of reactions over TiO_2 increases linearly with intensity, whereas at higher intensities the increase becomes dependent on the square root of intensity (10). At what point this change in dependence occurs has significance in the cost of building a concentrating solar system. The rate of mineralization of TCE was determined as a function of lamp intensity (Table 3). These limited data establish an increasing rate with increasing intensity but are not definitive in differentiating linear from square-root dependence. To develop an effective solar process for the treatment of contaminated water, it is essential to be able to extrapolate data obtained in the laboratory using artificial light sources that mimic outdoor conditions. Xenon arc and mercury-xenon arc lamps have been calibrated with a spectroradiometer, and the results are shown in Table 4. The artificial sources are much richer in the near-UV than is the terrestrial solar spectrum.

Immobilized forms of TiO_2 have been compared to the suspended form in order to evaluate the potential of supported forms for use in a solar water-decontamination system. Two supported forms have been tested. In the first, the DeGussa P25 TiO_2 was coated on glass beads and successive runs made with the same packed bed of catalyst. As is evident from Figure 1, the activity was roughly 20% less for the supported form or fixed bed versus the suspended form (0.15), and activity was maintained through 13 successive runs of about 6 h each. The second supported material tested consisted of TiO_2 on coated fiberglass mesh of varying degrees of weave density which was supplied by Nulite, a division of Nutech Energy Systems, Inc. These are only qualitatively described as a coarse, medium, and fine mesh (A, B, and C, respectively), and the nature of the TiO_2 coating is not identified by the supplier. The material was tested by supporting two layers of the material at a 45-deg angle to both the flow of the solution and the light beam. As can be seen from the results in Table 5, under these nonoptimized conditions the rates were about half of the rate for the suspended form of the catalyst.

DISCUSSION:

The results reported here establish that a common groundwater contaminant, TCE, can be destroyed by irradiating contaminated aqueous solutions that contain suspended or immobilized TiO_2 with light comprised of wavelengths in the solar spectrum. Other work at the Solar Energy Research Institute (SERI) includes development of data on system configuration and process cost. Key issues in the development of a solar process for treating contaminated water are to maximize the quantum yield for production of hydroxyl radical, to minimize the nonproductive reactions of hydroxyl radical, and to extend the effective wavelength of the semiconductor into the visible portion of the solar spectrum. Improvements in any combination of these areas will improve the effectiveness of the solar process.

The mineralization of TCE is accomplished under conditions that are readily achievable in a solar process. The increase in the apparent rate constant as initial concentration decreases is very favorable because concentrations found in groundwater contamination are frequently below 1 ppm. The relative insensitivity of the mineralization rate to pH that was observed in the preliminary experiments indicates that pH control would not be required in an actual process. The dependence of rate on increasing photon flux provides motivation for using a concentrating system in a solar process. The effectiveness of immobilized forms of TiO_2 found in this and other work (11) establishes that expensive catalyst addition and separation operations will not be required.

Work is under way to address the key issues in the development of a solar process for treating contaminated water. To do so will require a more detailed understanding of the mechanism for destruction of organic compounds over illuminated semiconductors.

Table 1. Rate of destruction of TCE as a function of initial concentration

[TCE] ₀	k
60 ppm	0.35 min ⁻¹
37	0.45
19	0.72
0.30	4.8, 1.4
0.30	4.1*

*Groundwater sample

Table 2. Rate of destruction of TCE as a function of pH ([TCE]₀ = 60 ppm; 0.05 N total phthalate ion)

pH	k
5.5	0.23 min ⁻¹
6.0	0.32
6.2	0.45
8.0	0.40

Table 3. Rate of destruction of TCE as a function of light flux (I₀ = 88.8 suns; [TCE]₀ = 60 ppm)

I/I ₀	k
0.90	0.32 min ⁻¹
0.49	0.16
0.13	0.10

Table 4. UV Power (300 - 400 nm) SERI Artificial Sources vs. Solar

Light Source	UV Power, W/m ²	"UV Suns" (quanta)
Sun, D.N., AM 1.5	22	1.00
1-kW Xe lamp, old	2240	86.6
1-kW Xe lamp, new	5980	230
1.6-kW Hg-Xe lamp, new	49300	1870

Table 5. Comparison of DeGussa P25 TiO₂ with TiO₂ immobilized on fiberglass cloth (Nutech) (1500 W Hg 1Xe arc lamp)

Mesh	k
A	0.19 min ⁻¹
B	0.33
C	0.47
P25 (0.1)	0.88

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MECHANISM OF THE PHOTOCHEMICAL DEGRADATION OF ORGANIC POLLUTANTS ON TiO_2

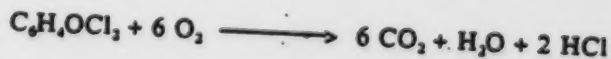
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ABSTRACT:

TiO_2 particles (in the anatase crystalline form) are known to be very effective photocatalysts in bringing about the complete mineralization of organic pollutants as complex as PCB's. However, the mechanism by which the pollutants are degraded on the particles is understood only in a few details. This paper will summarize the current knowledge concerning the mechanism of the TiO_2 process and describe some experiments carried out in our laboratory designed to provide further insight into the mechanism. These experiments show clearly that the primary oxidant is the hydroxyl $\text{OH}^\cdot$ radical and that these radicals are formed and react heterogeneously on the surface of the TiO_2 particles.

INTRODUCTION:

Although a number of water purification techniques are available, a group of new techniques, called Advanced Oxidation Processes, are receiving increasing attention. These processes rely on generation of short-lived oxidative radicals (often $\text{OH}^\cdot$ radicals) by photolysis or radiolysis. One of these processes involves the photolysis of TiO_2 particles (in the anatase crystalline form) using near UV light (300-400 nm). It is now well established that the TiO_2 process can bring about the complete mineralization of most of the organic pollutants found in natural and industrial water streams. For example, 2,4-dichlorophenol ($\text{C}_6\text{H}_4\text{OCl}_2$) reacts according to



In semiconductor photocatalysis several steps can be distinguished:

1. *Absorption of light by the semiconductor:* As shown in Figure 1, the absorption of a photon of light raises an electron from the valence band of the semiconductor into the conduction band, leaving a 'hole' (absence of an electron) in the valence band. In the case of TiO_2 , the energy separation (bandgap) between

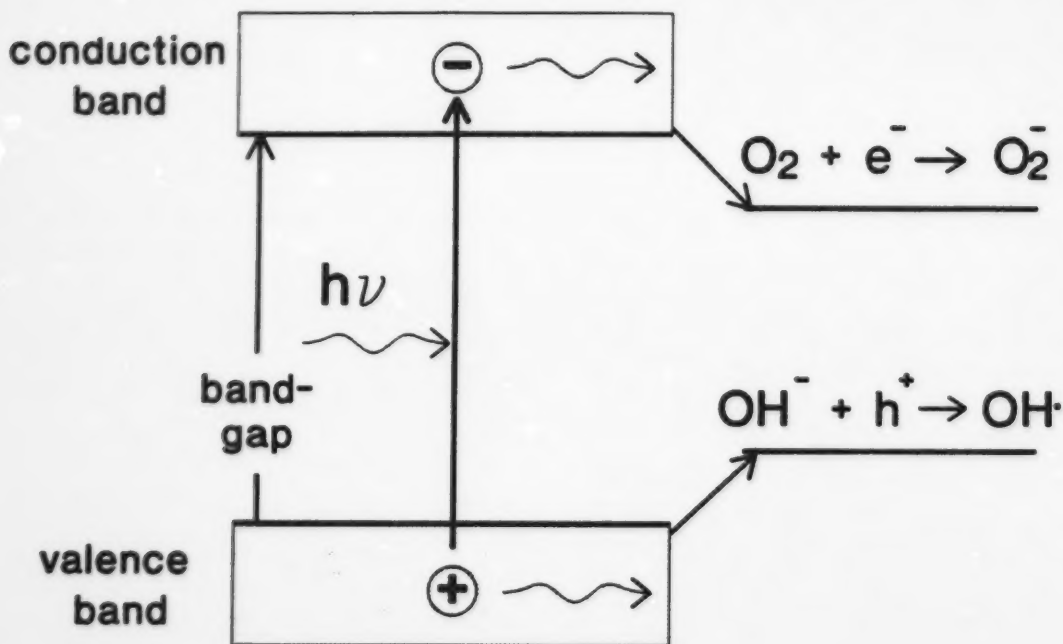


Figure 1 Energy bands and photochemical reactions for the photocatalysis process in TiO_2 (anatase).

the valence and conduction bands is ~ 3.2 eV. This means that only photons with a wavelength $\lambda < 390$ nm can be involved in this primary photochemical step.

2. *Migration or diffusion of holes and/or electrons to the surface of the particles:* If the particles are large enough, there will exist an electric field that favors migration of holes to the surface. However, in most cases the particle size is too small ($< 1 \mu\text{m}$), so that diffusion is the primary mechanism for movement of the electrons and holes to the surface. The subsequent fate and dynamics of these excess charge carriers are of considerable importance in the performance of devices based on semiconductor photocatalysis.

3. *Reaction of excess charge carriers with species on the surface:* Most oxide semiconductors, such as TiO_2 , when placed into an aqueous suspension, become covered with a high proportion of hydroxyl groups. Thus when holes diffuse to the surface, almost all of them react with the surface-bound hydroxyl groups to form $\text{OH}^\cdot$ radicals. Electrons that diffuse to the surface are strong reducing agents. If oxygen is present in the solution, a likely reaction is the reduction of oxygen to the superoxide ion $\text{O}_2^\cdot^-$.
4. *Chemical reactions on the surface:* The primary chemical species (in the TiO_2 case, $\text{OH}^\cdot$ and $\text{O}_2^\cdot^-$ radicals) then proceed to react with adsorbed substrates (pollutant molecules) to initiate a series of degradation reactions that lead ultimately to complete mineralization.

Naturally this demonstrated success in removing organic pollutants from water systems has stimulated interest in commercialization. In spite of several reports of product yields, very little is known about the mechanism of this photodegradation process. It is important to understand the details of this mechanism, not only as a strategy to improve yields, but also to identify the intermediates so as to evaluate their potential toxicity.

BACKGROUND:

Carey, Lawrence and Tosine (1) of the Canada Centre for Inland Waters were the first to recognize the potential of TiO_2 to act as a photocatalyst to degrade organic pollutants. They found that irradiation of TiO_2 suspensions with 365 nm light brought about the complete degradation of chloro-organic molecules as complex as PCB's. Oliver *et al.* (2) determined that the quantum yield for this process could be as high as 0.2. Carey & Oliver (3) found that the chlorine content of pulp mill black liquors could be reduced. Since then many papers have appeared, most of which have focussed on the UV irradiation of TiO_2 aqueous suspensions and the determination of the rates of formation of $\text{Cl}^\cdot$ and/or CO_2 , or the disappearance of starting material, for a wide range of pollutants including chloroalkanes, chloroalkenes, chlorophenols, PCB's and a variety of non-chlorinated organics such as benzene and benzoic acid. Generally it has been found that the kinetics obey the Langmuir-Hinshelwood kinetic model (4) thus suggesting that the reaction is occurring on the surface of the TiO_2 particles (5). Ollis (6), Oliver and Cary (7), Langford and Cary (8), Serpone (9) and Ollis, Pelizzetti and Serpone (10) have reviewed this research area.

Although aqueous TiO_2 suspensions are suitable for model studies, such suspensions would not be practical for a commercial process because of the problem of separation of the suspended

particles. Thus there has been considerable interest in immobilizing the particles on some fixed substrate (usually glass). For example, Serpone *et al.* (11) embedded TiO_2 particles onto glass beads and found a high photocatalytic activity. Skala *et al.* (12) and Xu *et al.* (13) employed a reactor, developed by Nulite, consisting of TiO_2 particles embedded onto a glass mesh. They found good reaction rates in this system for the photodegradation of chloroaromatic compounds. Matthews (14) reports high photodegradation rates on a similar type of reactor.

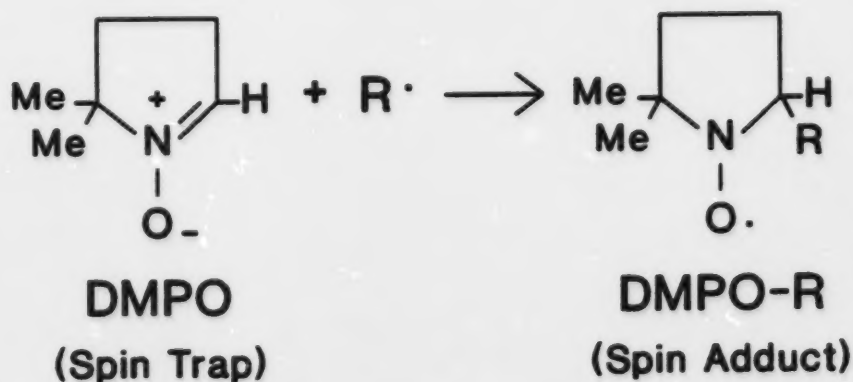
THE EPR SPIN TRAPPING METHOD:

Our approach to this problem has been to utilize the technique of spin trapping, with detection by electron paramagnetic resonance (EPR) spectroscopy [also called electron spin resonance (ESR) spectroscopy], to identify and characterize the reactive radicals produced on the surface of the TiO_2 particles.

EPR spectroscopy is a technique that is sensitive to the presence of molecules with unpaired electrons (such as free radicals) (15). The technique is very sensitive ($< 10^{-9}$ M free radicals can be detected). However, the radical intermediates produced in the TiO_2 photocatalysis reaction are too short-lived to be detected directly by EPR. In favorable cases this problem can be alleviated by the use of the *spin trapping* technique (16).

The addition of compounds called *spin traps* (usually nitrones), converts reactive radicals into relatively stable nitroxide radicals (*spin adducts*), which can be detected by EPR (see scheme 1). For example, phenyl-*t*-butyl nitron (PBN) and

Scheme 1

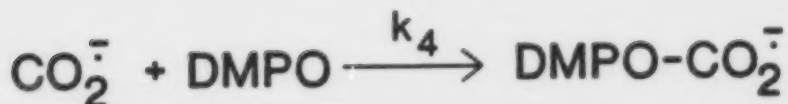
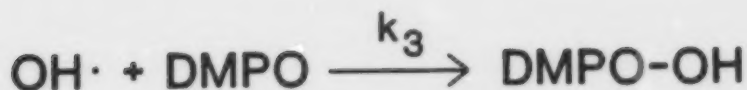
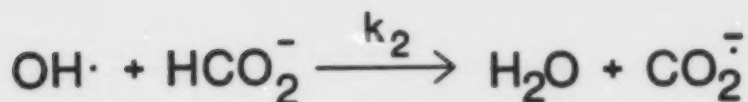
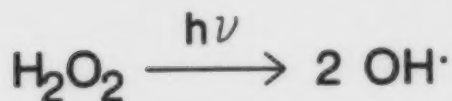


5,5-pyrroline-N-oxide (DMPO) are popular as spin traps. Jaeger and Bard (17) were the first to provide evidence for the intermediacy of oxygen centered radicals in the photolysis of TiO_2 aqueous suspensions; they detected the $\text{OH}^\cdot$ radical spin adduct by EPR with PBN as spin trap. However, the detection of the $\text{OH}^\cdot$ spin adduct by EPR does not necessarily prove the presence or intermediacy of $\text{OH}^\cdot$ radicals in the photocatalytic reaction, as there are other known reactions, not involving $\text{OH}^\cdot$ radicals, that may lead to the same spin adduct. Therefore it is mandatory to carry out additional experiments to confirm the identification of $\text{OH}^\cdot$ radicals.

In previous work on the photochemistry of hydrogen peroxide, benzoquinone and other reactions (18) we have developed a protocol, based on a competition reaction with formate, to test for the presence of free $\text{OH}^\cdot$ radicals in solution. Scheme 2 shows the important reactions in the formate competition system. Our standard for a truly homogeneous source of $\text{OH}^\cdot$ radicals is the well-known photolysis of H_2O_2 (18a), which, on the addition of DMPO produces a clean EPR spectrum of the DMPO- $\text{OH}^\cdot$ spin adduct. When formate is added to the solution, the formate competes with DMPO for the $\text{OH}^\cdot$ radicals generating $\text{CO}_2^\cdot$ radicals, which themselves get trapped by DMPO to form the DMPO- $\text{CO}_2^\cdot$ spin adduct. As the concentration of formate is varied the ratio (R) of the concentrations of the DMPO- $\text{OH}^\cdot$ and DMPO- $\text{CO}_2^\cdot$ adducts may be followed by EPR since the two EPR spectra are quite different. We define a 'cross-over point' (COP) as the point where R becomes unity.

In any test system, if $\text{OH}^\cdot$ radicals react in a homogeneous aqueous phase, the behavior in a formate competition experiment *must be the same as that of the H_2O_2 system*. In our experiments on the TiO_2 system (19) we have applied our spin-trapping test for free $\text{OH}^\cdot$ radicals to examine whether $\text{OH}^\cdot$ radicals are formed and react heterogeneously on the surface of the TiO_2 particles or alternatively if they diffuse into solution and then react homogeneously with substrates.

Scheme 2



RESULTS AND DISCUSSION:

Figure 2a shows the EPR spectrum of the DMPO adduct of the $\text{OH}\cdot$ radical obtained after photolysis of a degassed buffered solution (pH 7, 1 mM phosphate) of DMPO (1 mM) and hydrogen peroxide (2%). The sample was illuminated for 25 s. The spectrum shows only four lines with an 1:2:2:1 pattern of the intensities, which arises from the fact that in the case of the DMPO-OH adduct the hyperfine splitting constants for the nitrogen and the β hydrogen are the same ($a_N = a_H = 14.9$ G). The same DMPO-OH spectrum was obtained by UV illumination of a degassed suspension of TiO_2 (anatase) particles in the same phosphate buffer with DMPO (1 mM).

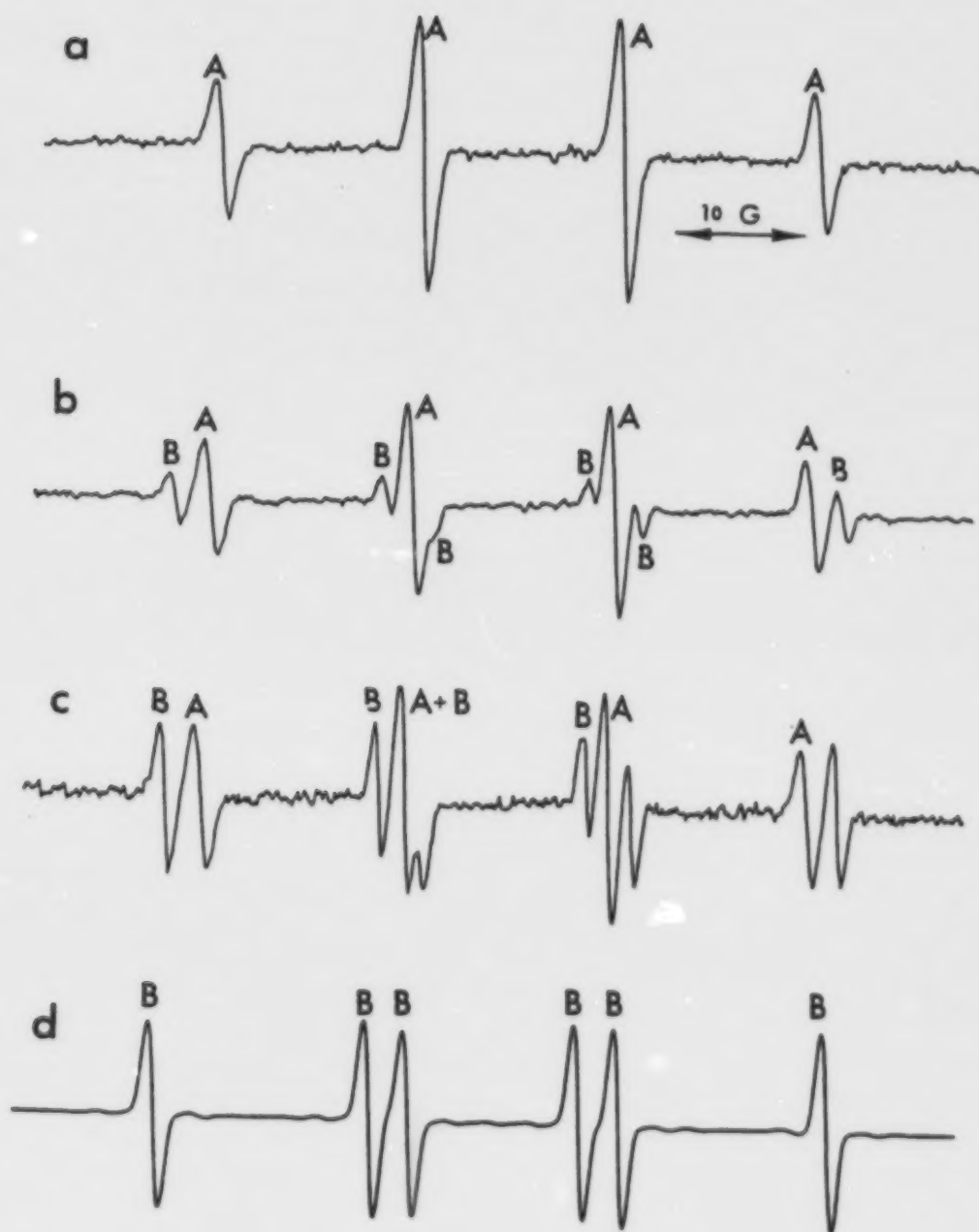


Figure 2 EPR spectra of spin adducts formed by the UV photolysis of H_2O_2 or TiO_2 in an aqueous medium containing 1 mM DMPO at pH 7. (a) No additional components; (b) 0.5 mM sodium formate added; (c) 1.0 mM sodium formate added; (d) 10 mM sodium formate added. [microwave power 20 mW; modulation amplitude 1 G]

After UV irradiation of a sample (degassed hydrogen peroxide buffer solution or titanium dioxide suspension) with additional excess formate (10 mM), no DMPO-OH can be detected. Instead the EPR spectrum of the DMPO-CO₂⁻ spin adduct appears (Figure 2c). In this case the two hyperfine splitting constants are different ($a_N = 15.6$ G, $a_H = 18.7$ G) and six lines with equal intensities are obtained.

Figure 2c shows the EPR spectrum of degassed buffer solution at a formate concentration close to the COP (vide infra). In this case the spectrum is a superposition of the spectra of DMPO-OH (Figure 2a) and that of DMPO-CO₂⁻ (Figure 2d).

Figure 3 shows the results of the formate competition experiment with hydrogen peroxide (curve a) and titanium dioxide (curve b). The concentrations of buffer, DMPO, H₂O₂ (or TiO₂) are kept constant. NaCl has been added to keep the ionic strength constant. With an increasing amount of formate a larger fraction of the [•]OH radicals react with formate and not with DMPO; this results in an increased formation of the DMPO-CO₂⁻ spin adduct and a decreased amount of the DMPO-OH spin adduct. As the rate constants k_1 and k_2 are the almost the same, the COP is near to the point where the concentrations of DMPO and formate are equal, i.e. the ratio of the concentrations (R-value) is 1. The reference system with H₂O₂ shows exactly the expected behavior with reactions of free [•]OH radicals. In the case of the TiO₂ suspension, however, the COP is already reached at a concentration of formate of only 0.7 M.

As a model pollutant we have used 4-chlororesorcinol (4-CR). When this compound is added to a TiO₂ suspension containing DMPO, the DMPO-OH spectrum decreases in intensity as the concentration of 4-CR increases. This is a clear indication that the 4-CR is reacting with the OH[•] radicals; however, the product of that reaction is apparently unreactive towards DMPO. Figure 4 shows the DMPO-OH EPR signal amplitude as a function of the concentration of 4-CR. From the concentration of 4-CR that reduces the DMPO-OH EPR signal amplitude by one half, it is possible to obtain the relative rate constants for the reaction of OH[•] radicals with DMPO or 4-CR. In this case it is clear that the 4-CR is reacting more rapidly with OH[•] than does DMPO.

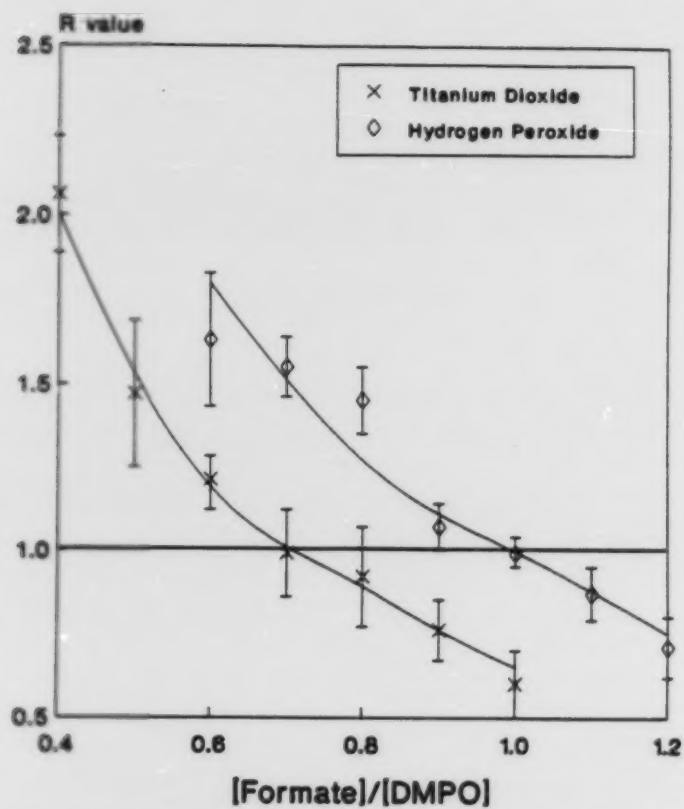


Figure 3 Formate competition COP analysis. R is the ratio of the peak heights of the DMPO-OH to the DMPO-CO₂ spin adducts.

CONCLUSIONS:

The EPR spectra obtained after UV irradiation of the H_2O_2 solution and the TiO_2 suspension are identical and must arise from trapping the same radical intermediates. The uniqueness of the DMPO-OH spectrum enables an assignment beyond any doubt. However, the presence of DMPO-OH does not necessarily prove the presence or intermediacy of $\cdot\text{OH}$ radicals in the photocatalytic reaction, as mentioned above. The formate competition reaction has demonstrated that $\text{OH}\cdot$ radicals are the primary intermediate in the TiO_2 photolysis reaction. However, the different behavior, with respect to the R factors, provides strong evidence that the $\text{OH}\cdot$ radicals are generated and react heterogeneously on the surface of the TiO_2 particles.

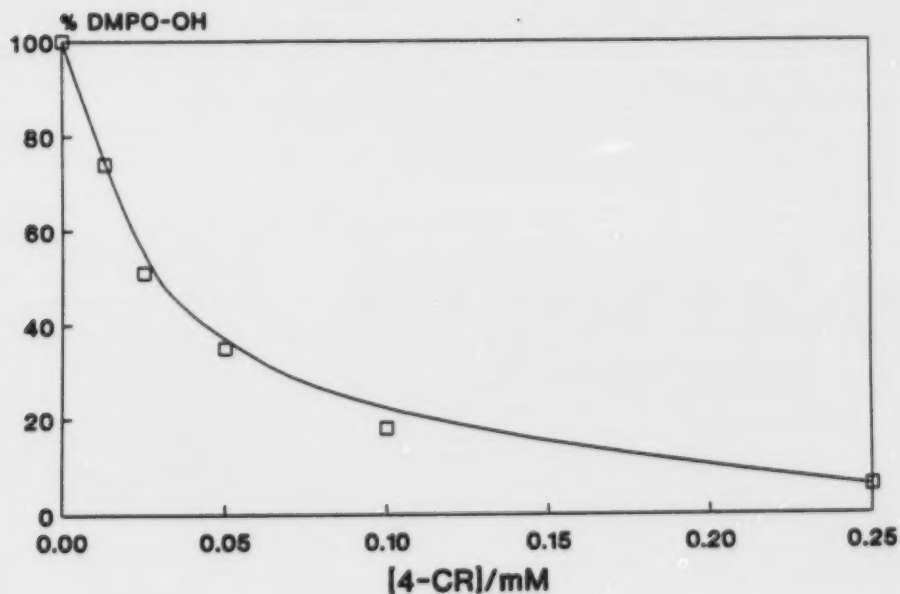


Figure 4 Relative amplitude of the DMPO-OH spin adduct as a function of the concentration of 4-chlororesorcinol in the TiO_2 UV photolysis system. The concentration of DMPO is 1 mM.

The spin trapping method we have developed has been applied to the study of a model pollutant, 4-chlororesorcinol. The results indicate that $\text{OH}^\bullet$ radicals on the surface of the TiO_2 particles react directly with 4-chlororesorcinol at a rate which is faster than that with DMPO. These experiments have demonstrated that it is possible to study the primary reactions in the TiO_2 system and obtain relative rate constants. Extension of these experiments should allow the determination of relative rate constants for a variety of pollutant molecules.

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SESSION 3
PRODUCT DEVELOPMENT
AND EMERGING TECHNOLOGIES

**ADVANCED TECHNOLOGY FOR DESTRUCTION OF ORGANIC
POLLUTANTS BY PHOTOCATALYSIS**

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ABSTRACT:

The TiO_2 photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) pentachlorophenol (PCP) and nitrobenzene (NB) was examined using a prototype photoreactor fabricated by Nulite. The degradation of both pollutants proved very efficient as in 12 min it was possible to bring the concentration of 2,4-DCP from 10 to 0.5 ppm and in a separate experiment the concentration of PCP from 100 to 0.5 ppb. The effect of flow rate on the degradation of 2,4-DCP in both single pass and multi-pass operation modes was investigated. In single pass experiments, the conversion (%) of 2,4-DCP initially decreases with increasing the flow rate reaching a plateau at about 1-1.5 L/min. This indicates that the reactor operates more efficiently at higher flow rates. In the multi-pass experiments, the degradation rate of 2,4-DCP increases non-linearly with the flow rate. The effect of concentration (1.2 - 20 ppm) on the degradation of 2,4-DCP was also investigated. In contradiction with the first order reaction in homogeneous solutions, the degradation rate of 2,4-DCP increases and the degradation rate constant decreases with increasing concentration of 2,4-DCP. the results are explained in terms of surface heterogeneity of TiO_2 . Partial removal of oxygen through the introduction of nitrogen just before the photoreactor decreased the degradation rate remarkably. However, introducing oxygen or air increased the degradation rate considerably. The addition of hydrogen peroxide improved the degradation rate of 2,4-DCP and NB dramatically.

INTRODUCTION:

Rising public concern is causing increasing government regulation concerning toxic pollutants while previous disposal methods are becoming limited by the decreasing availability of sites and the awareness of their limited containment ability. The U.S. Environmental Protection Agency (E.P.A.) recognizes only air stripping and carbon adsorption as "most effective

treatments for water purification" (1). Unfortunately, air stripping simply removes the volatile organic pollutants from the water only to place them in the atmosphere, while the carbon adsorption process creates filters of hazardous solid waste which then must be disposed of. As both of these technologies become subject to new and more stringent regulations, the demand for a destructive purification technology will become a matter of tantamount importance.

The complete mineralization of a broad range of halogenated hydrocarbons into carbon dioxide, water and mineral acid HX, mediated by illuminated TiO_2 , is very well documented in the literature e.g. references (2-7). Nulite, with the financial support of the National Research Council of Canada, the Ontario Ministry of the Environment and Nutech Energy Systems Inc., is currently conducting intensive research to develop this photocatalytic process into a commercially viable technology for water treatment (8-10). Prototype photoreactors, fabricated by Nulite, are being tested at various academic and industrial laboratories.

EXPERIMENTAL:

General Procedure

Reactors, fabricated by Nulite, were used throughout this study. These photoreactors are comprised of a stainless steel jacket, a lamp and a photocatalytic sleeve (Figure 1). The lamp emits ultraviolet light in the 300-400 nm range and is mounted coaxially within the jacket. Around the lamp lies a sleeve formed of fibreglass mesh that is coated with titanium dioxide (anatase). The TiO_2 is activated by ultraviolet light. Contaminated water flows through the fibreglass mesh parallel with the lamp. Typically, 3 L of 10 ppm of 2,4-dichlorophenol (2,4-DCP), solution was circulated through the system for 15 min in the dark. At this point the light was switched on and samples were taken periodically. The samples were analyzed on a Hewlett Packard 5890A gas chromatograph using a megabore DB-5 column (30m long, 0.53 mm diameter) with an electron capture detector operating at 300°C. The injection port temperature was held at 250 °C and nitrogen (14mL/min) was used as carrier gas. For pentachlorophenol analysis, the known acetylation/extraction technique was used.

RESULTS AND DISCUSSION:

The TiO_2 Photocatalytic Degradation Reactions

The degradation of 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) were chosen to test the prototype photoreactors for a number of reasons: (1) earlier studies suggested that complete mineralization of these compounds, mediated by illuminated TiO_2 is possible, (2) being aromatic molecules, they represent one of the main classes of environmentally important pollutants for which this technology is designed; and (3) being chlorinated compounds, they can be accurately detected with an electron capture detector.

The photocatalytic degradation of 30 mg (3 L at 10 ppm) 2,4-DCP in aerated aqueous solution was investigated in a continuous recirculation mode at a flow rate of 4L/min as a function of irradiation time. Before irradiation, the solution was recirculated through the reactor for 15 min in the dark. The results (Figure 2) clearly show that the reaction proceeds very efficiently since, in 12 min, it was possible to bring the 2,4-DCP concentration from 10 to 0.5 ppm (i.e., 95% degradation).

The photocatalytic degradation of 300 μg (3 L at 100 ppb) PCP was examined under conditions similar to those used for 2,4-DCP. As in the 2,4-DCP reaction, the process is very efficient (Figure 2) and in less than 15 min it was possible to reduce the concentration of PCP from 100 ppb to the recommended environmentally acceptable level of <0.5 ppb (i.e., 99.5% degradation).

The photocatalytic degradation effectiveness of this reactor has been demonstrated for other organic pollutants in an experiment modeled on the composition of leachate from a landfill site in the township of Gloucester outside the city of Ottawa, Canada. The Gloucester ground water leachate was found to contain benzene, toluene, chlorobenzene, trichloroethylene, 1,1-dichloroethylene, diethylether, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane and chloroform. The degradation of these organic pollutants in a model solution containing 2.5 ppm of each of the pollutants was examined and found to be effective (8). The degradation of the Gloucester water compounds acquires special importance, not only because of the large number of organic pollutants tested individually or in an equimolar mixture, but also because the Gloucester water contains organic compounds belonging to diverse classes of organic pollutants which are of the greatest environmental concern today.

We are currently focusing on the investigation of various experimental parameters to optimize the performance of the reactor. Obviously, these investigations are required before pilot scale testing and economic evaluation can begin. Results are very promising.

Effect of Concentration

The effect of initial concentration (1.2-20ppm) of 2,4-DCP on the degradation rate was investigated and the apparent rate constant (k) was found to decrease with concentration (Figure 3). This is in contradiction with first order reaction kinetics for homogeneous solutions and clearly argues in favour of surface reactions.

Reaction at the TiO_2 surface, where initial concentration is low, approximate first order kinetics. The rate is then determined by equation (1).

$$\text{rate} = k [2,4\text{-DCP}] \quad (1)$$

Using the k values determined earlier, the rates were calculated and were found to increase with increasing initial concentration. A graph of the rate vs the concentration (Figure 3) closely approximates the Langmuir isotherm which is also indicative of a surface reaction.

Effect of Flow Rate

The effect of flow rate of a continuously recirculated 2,4-DCP solution (10 ppm) on the degradation rate was also investigated. Figure 4 indicates that the degradation rate constants increase non-linearly with the flow rate. This may be attributed to a higher flow maintaining a higher concentration of pollutant on the TiO_2 surface by simultaneous replacement of the degraded 2,4-DCP molecules.

In another set of experiments it was required to assess the effect of flow rate on the degradation of 2,4-DCP in a single pass operation mode. Figure 5 illustrates the conversion (%) of 2,4-DCP vs flow rate. The data indicate that the conversion decreases with increasing flow rate, reaching a plateau at about 1-1.5 L/min. This means that the reactor operates more efficiently at higher flow rates (relative efficiency = conversion (%) x flow rate). A linear relationship is obtained when the relative efficiency is plotted vs flow rate. It was determined that 32% degradation of 2,4-DCP was achieved when a single reactor was operated at 1 L/min flow rate in a single pass mode. However, to achieve efficient degradation (> 95%) several reactors should be linked in a series mode. While the work is still in progress, the results seem very promising.

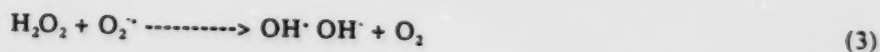
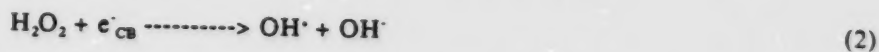
Effect of Oxygen

All previous testing had been conducted in open atmosphere systems. To examine oxygen's effect, the solution in the reservoir was exposed to an oxygen bubbler both before and during irradiation. This solution saturation approach yielded no difference in rate. An alternative method of oxygen introduction was devised so that it entered into the line to the reactor. Adding gas to the system slowed the solution flow rate from 3 to 2 L/min. Previous open system conditions produced a rate of 0.12 min^{-1} which was reduced to 0.03 min^{-1} by introducing nitrogen. However, the degradation rate was increased by 80% in comparison with the open conditions through the addition of oxygen. Similar results were obtained when air instead of oxygen was introduced into the line to the reactor.

Electron-Hole Recombination

One of the major practical problems of semiconductors as photocatalysts is the electron-hole recombination process of the photogenerated electron-hole pair. The overall result of its occurrence is merely the generation of heat. This process decreases significantly the photocatalytic activity of an excited semiconductor. The reported quantum yield for the TiO_2 photocatalytic degradation of various organic compounds varies between 1-3%. Thus, decreasing the contribution of the electron-hole recombination process is of paramount importance if a commercial application is desired.

One possible solution is to add irreversible electron acceptors to the reaction. These additives, once they accept the electron from the conduction band or the superoxide ion ($\text{O}_2^{\cdot -}$), should undergo dissociation leaving no need for a secondary disposal process. They should provide additional routes for OH radical formation. Hydrogen peroxide is an example. When H_2O_2 accepts an electron it will dissociate according to the following equations:



This will not only prolong the lifetime of the valence band "hole" but also provides an additional route for OH radical formation. We have found, for instance, the addition of H_2O_2 enhanced by the degradation rate of 10 ppm 2,4-DCP by a factor of two and that of 60 ppm nitrobenzene by a factor of five.

CONCLUSIONS:

Heterogeneous photocatalysis appears to have potential as a commercially viable technology for water purification. Our results clearly show that the TiO_2 photocatalytic degradation of a wide variety of organic pollutants is a highly efficient process. It is further demonstrated that the process is a surface phenomenon and as such is influenced by the pollutant concentration and the flow rate. Oxygen was found to be a major factor in this photocatalytic process. We are presently focusing on the investigation of various engineering parameters to optimize the performance of the reactor. The results provide a strong promise of a clean, inexpensive and simple process to remove organic pollutants from natural and industrial water system.

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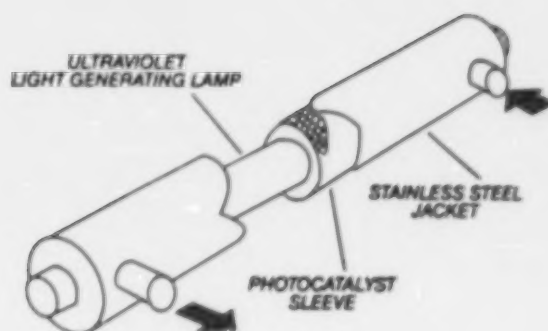


Figure 1: Nulite's Photoreactor

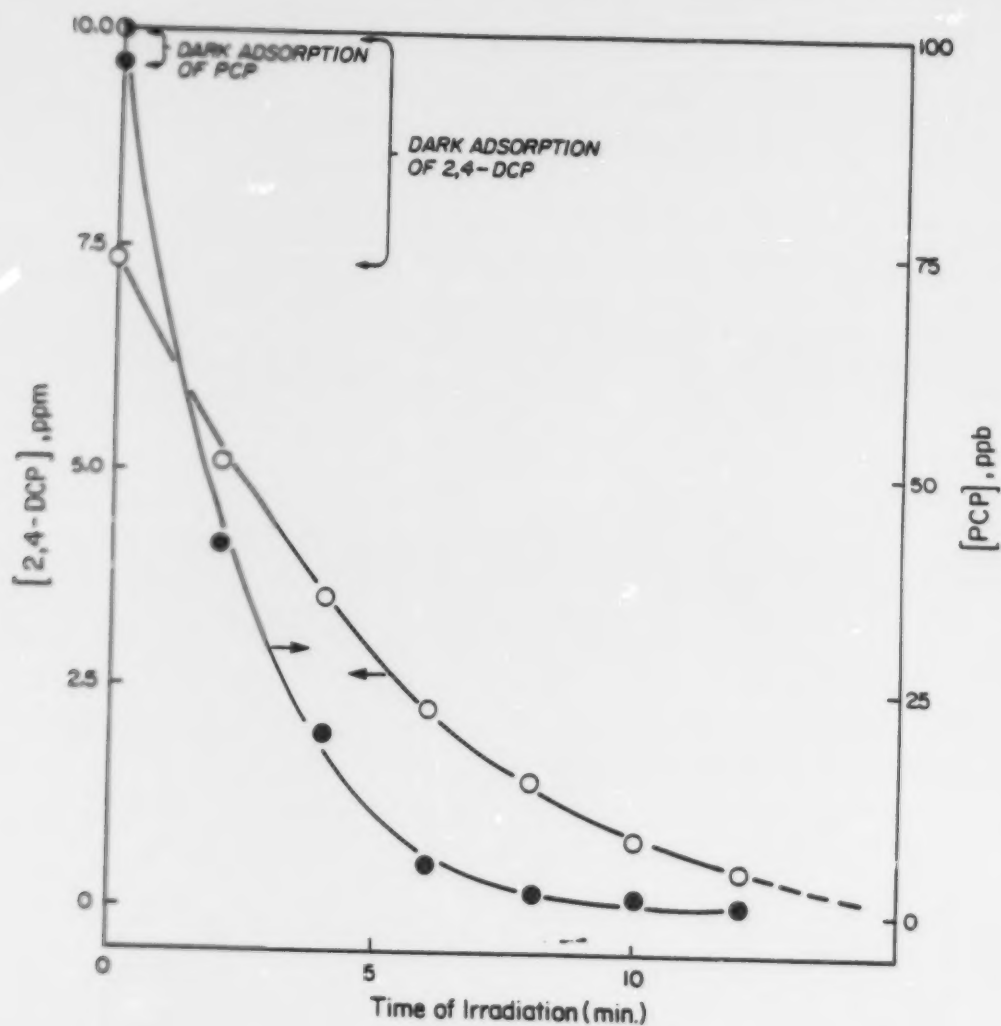


Figure 2: Plot showing changes in the concentrations of 2,4-DCP (O) and PCP (●) as a function of irradiation time in a continuous recirculation mode at 4 L/min flow rate.

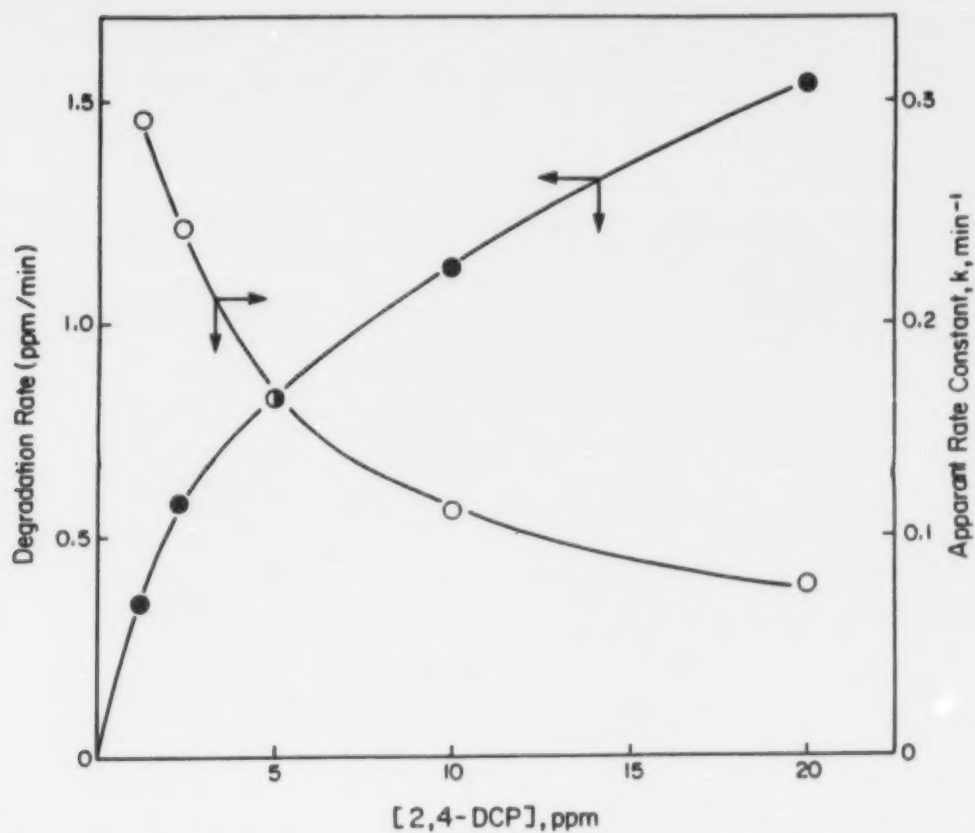


Figure 3: Effect of the initial concentrations on the degradation rate and the degradation rate constant of 2,4-DCP. Flow rate = 3 L/min; initial concentrations are 1.2, 2.4, 5, 10 and 20 ppm.

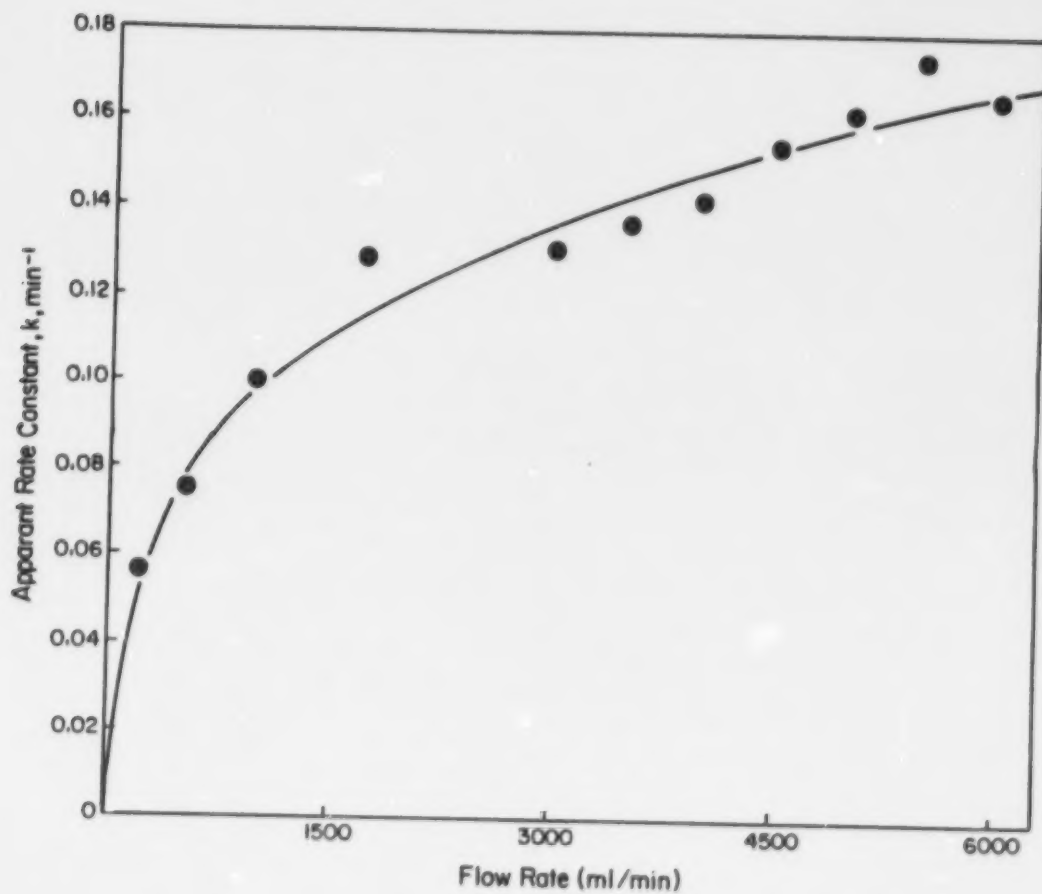


Figure 4: Effect of flow rate on the degradation rate constant of 2,4-DCP.

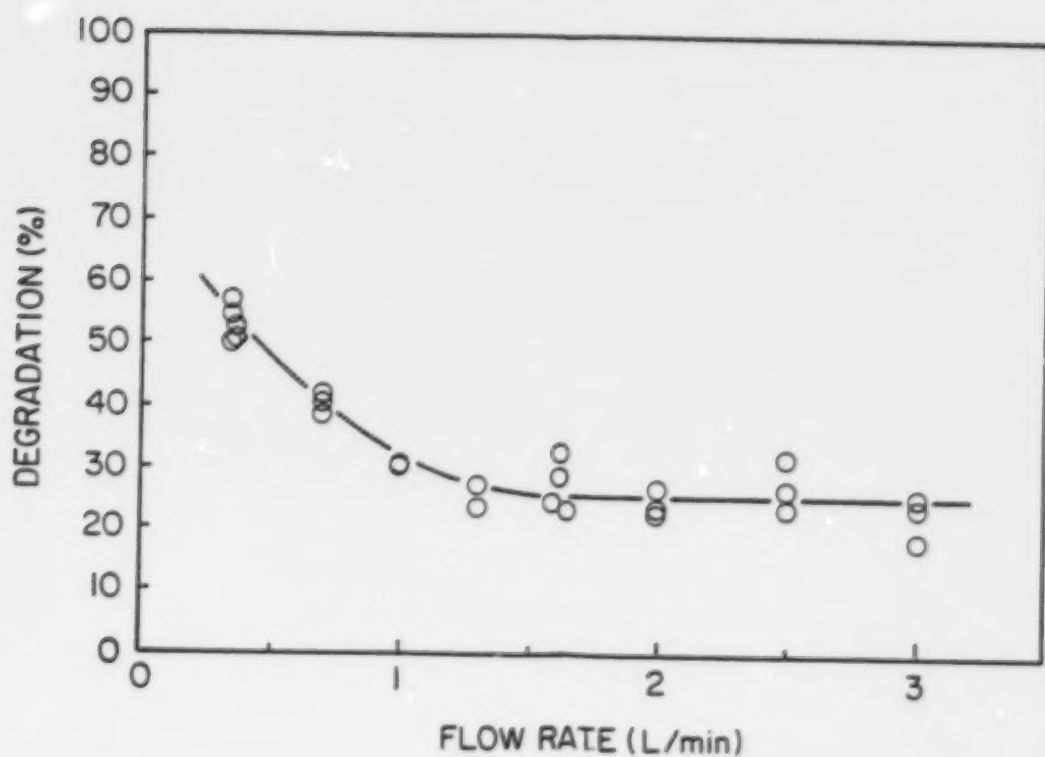


Figure 5: Plot showing the effect of flow rate on the conversion (%) of 2,4-DCP in the outlet stream of the reactor in a single-pass mode. Initial concentration = 10 ppm.

APPLICATIONS OF PHOTOCATALYSIS TO PESTICIDE RESIDUES IN THE FIELD

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ABSTRACT:

California rice fields annually receive major applications of pesticides. Laboratory tests showed that rice herbicides such as thiobencarb (Bolero¹) were photooxidized efficiently under solar UV irradiation in the presence of TiO_2 or ZnO , while uncatalyzed oxidation was very slow. *p*-Chlorobenzoic acid was the principal degradation product. Limited field tests with ZnO reduced thiobencarb levels by 90%, but a full-scale commercial test was somewhat less successful. While ZnO provides a means to limit adverse effects of accidental spills or overapplication of pesticides, it might be unsatisfactory for routine removal of pesticide residues from field water.

INTRODUCTION:

California accounts for about one-fourth of all pesticide use in the United States. In 1988, California agriculture and related industries consumed about 5 million kg of active pesticide ingredients (a.i.) (CDFA, 1990), and, not surprisingly, their residues appeared widely in field waters of the state.

Rice is a billion-plus dollar crop in Northern California; in a recent year, over 220,000 ha of land was utilized by flooded rice fields. A total of 2,105,000 kg of pesticide a.i. was used by the California rice industry in 1988, of which over 1,236,000 kg represented only 9 organic chemicals (Table 1)(CDFA, 1990). Even in normal use, this volume of application has been implicated in fish kills, destruction of other aquatic wildlife, and off-taste in public drinking water; unmeasured misapplication, spills, and waste disposal must account for additional burden.

¹ Bolero is a registered trade mark.

Table I. Major Rice Pesticides (CDFA, 1990).

Pesticides	Kg Applied	Ha Treated
Bentazon	118,252	102,146
Carbaryl	25,358	12,417
Carbofuran	26,770	23,852
2,4-D salts and esters	6,275	8,916
MCPA salts	105,925	114,598
Methyl parathion	32,512	42,447
Molinate	689,025	146,905
Propanil	36,215	7,622
Thiobencarb	195,924	45,165
TOTAL	1,236,256	

Most pesticides are applied by aircraft to the flooded rice fields in early summer when sunlight intensity is highest. Photooxidation provides the most important natural route for pesticide degradation in field water (Crosby, 1983). Present evidence suggests that hydroxyl radicals are involved in such oxidations (Draper and Crosby, 1981, 1984), and the capability to increase field oxidant levels rapidly but temporarily might allow the control of unwanted residues. Semiconductor-catalyzed or enhanced photooxidation has recently attracted considerable attention (Fox, 1983; Draper and Crosby, 1987) and appeared as an attractive candidate for field studies.

HERBICIDE PHOTODEGRADATION:

Most California rice pesticides are herbicides applied for aquatic weed control. The photodegradation of many of these in natural sunlight has been described previously (Crosby, 1983). Thiobencarb [*S*-(4-chlorophenyl)methyl-*N*, *N*-diethylcarbamothioate, I], sold under the trade name of Bolero®, is a particularly persistent major-use herbicide. It is applied for control of barnyard grass (*Echinochloa crus-galli*), a particularly troublesome weedy grass, and has become a mainstay of the rice industry in the U.S. and other rice-producing nations. It is only

slightly soluble in water (30 mg/L, 1.16×10^{-4} M), of low volatility (Henry's law constant 7×10^{-7}), and its low ultraviolet (UV) absorption at 300 nm ($\epsilon = 100$) strongly suggests that it should have only low photoreactivity at best.

Indeed, in distilled water solution irradiated in a sunlight-simulating photoreactor (Crosby, 1979), thiobencarb showed little degradative loss (Draper and Crosby, 1981). In UV-irradiated field water, it was slowly degraded by natural photooxidants (Ross and Crosby, 1985) to form a variety of photooxidation products (Draper and Crosby, 1981) including p-chlorobenzyl alcohol and p-chlorobenzoic acid. Monitoring of a commercial field application of thiobencarb, applied as Bolero® 10G formulation, likewise showed slow dissipation and the formation of the above products (Crosby and Bowers, 1980).

CATALYZED PHOTOOXIDATION:

Examination of the influence of 10 different known photooxidants, including inorganic nitrates and nitrites, acetone, hypochlorite, titanium dioxide, zinc oxide, and others, showed that the metallic oxides offered the most promise for increasing the photodegradation rate of thiobencarb. Starting with distilled water solutions containing 12 mg/L of thiobencarb and 100 mg/L of insoluble solid catalyst, irradiation with simulated solar UV energy at wavelengths longer than 290 nm caused essentially complete degradation of the herbicide within a little more than two hours; neither dark controls nor catalyst-free controls showed appreciable loss of thiobencarb (Fig. 1). Zinc oxide (ZnO) was as effective as titanium oxide (TiO_2).

Isolation and identification of degradation products was accomplished by collection from solutions onto solid-phase extraction cartridges followed by gas-chromatography mass-spectrometry with and without derivatization and by high-pressure liquid chromatography (HPLC). In samples taken part way through an irradiation experiment, principal products included p-chlorobenzyl mercaptan (II), p-chlorobenzyl alcohol (IV), p-chlorobenzaldehyde (V), p-chlorobenzoic acid (VI), and unspecified isomers of ring-hydroxylated thiobencarb (VII) (Fig. 2). At short reaction times, the transient thiobencarb sulfoxide (III) also could be detected. By the end of the irradiation period, only p-chlorobenzoic acid remained.

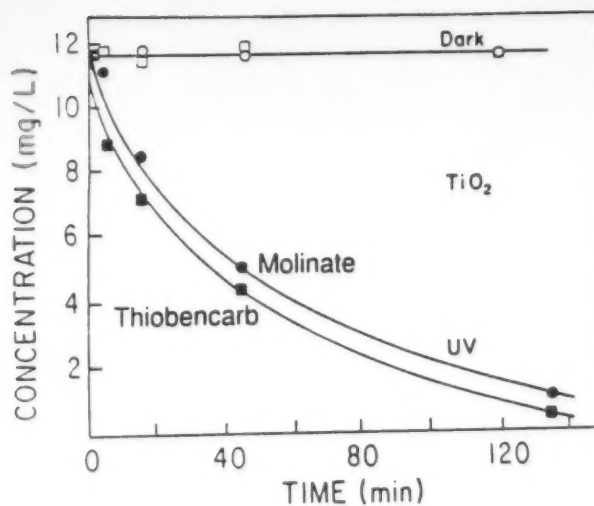


Fig. 1. Photooxidation of Thiobencarb catalyzed by TiO_2 . Photooxidation of the herbicide molinate was included for comparison.

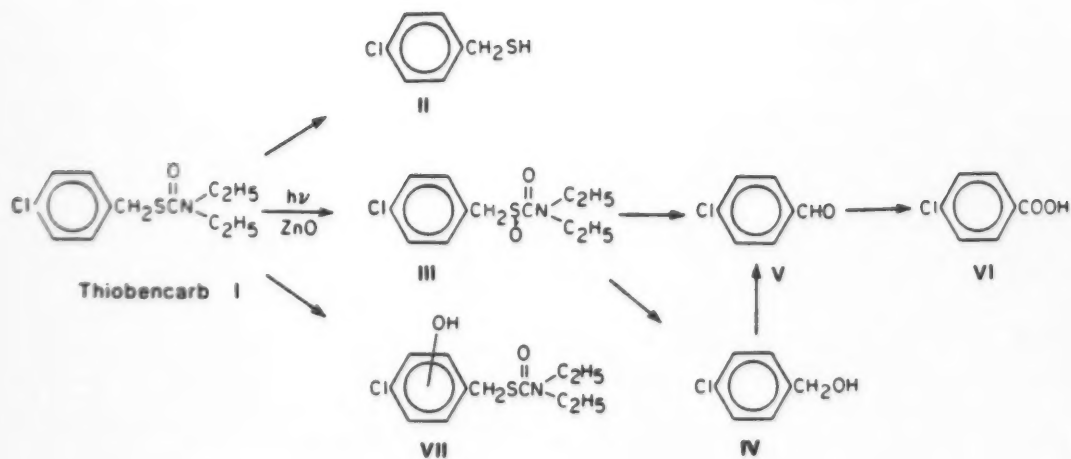


Fig. 2. Photodegradation products from thiobencarb in the presence of ZnO .

FIELD EXPERIMENTS

Small-scale field experiments were conducted at the UC-Davis Rice Research Facility. Bolero® 10G was applied by backpack sprayer at a rate of 6.3 kg/ha a.i. to 4.5 m² test plots in a flooded rice field. After 3 days, during which water was sampled at regular intervals, a pure grade of commercial ZnO suspended in water (1 g/L) was sprayed onto the water surface at rates of 0, 3, 6, and 12 kg/ha (measured as Zn). Thiobencarb levels, measured by gas chromatography, initially increased to about 1.2 mg/L (Fig. 3); addition of the ZnO caused a very rapid loss of herbicide, roughly proportional to the ZnO applied. Even though the reaction of thiobencarb was rapid, the initial minimum was maintained only briefly; as herbicide continued to be released slowly from the granular formation, the concentrations rose again slightly but remained as low as 20% of control values.

ZnO emerged as the photocatalyst of choice. First, it, itself, was degraded in sunlight to produce soluble Zn ion; this was the reason that its catalytic effect was transitory. Conversely, TiO₂ was persistent to the extent that efficacy of later pesticide applications would be jeopardized. ZnO

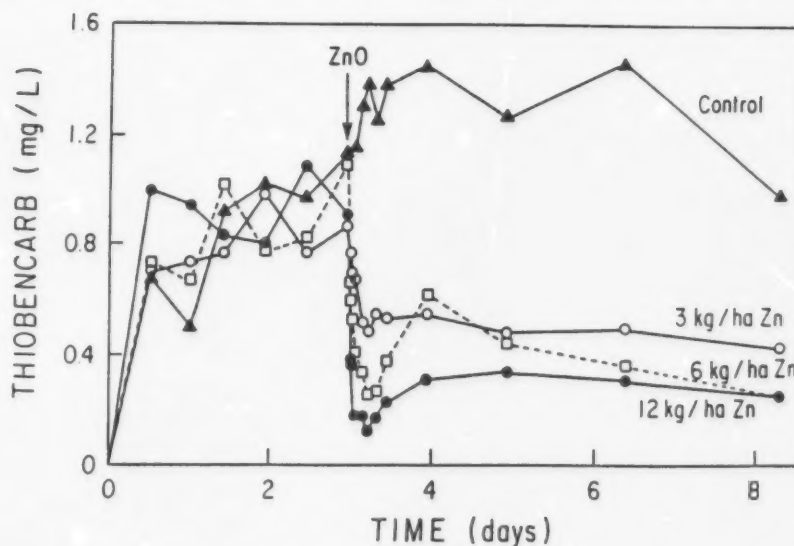


Fig. 3. ZnO-catalyzed photooxidation of thiobencarb in 4.5 m² field plots.

also was readily available in quantity at reasonable cost in a pure agricultural grade for plant nutrition. It was uniformly suspendable in water and could readily be sprayed.

A full-scale field test was attempted. Bolero ® 10G was applied commercially to 7-acre (2.8 ha) rice fields in the vicinity of Sacramento, CA; the water was analyzed before and after the application. About 6 days following herbicide application at 4 lbs/acre (4.5 kg/ha), an aqueous slurry containing 1 lb/gal (120 g/L) of ZnO was applied by aircraft at a rate of 4.5 and 9 kg Zn/ha, and the field water was sampled at intervals and analyzed for thiobencarb. Satisfactory results were observed in treated fields (Fig. 4), but no significant difference was seen between application rates. Control results were erratic, and values in Fig. 4 are averaged estimates. Simultaneous toxicity tests in caged fish, tadpoles, snails, and crustaceans showed no ill effects, and soluble Zn levels in the treated field water quickly returned to normal after a brief (24 hr) peak at 1 mg/L.

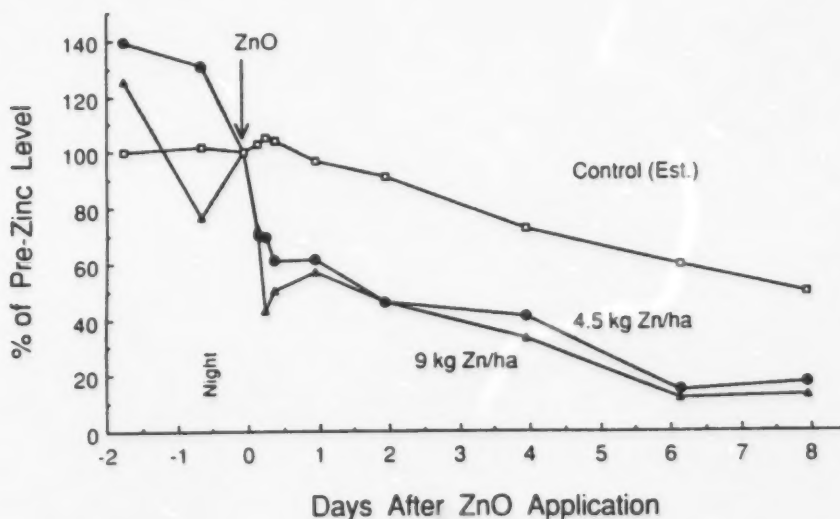


Fig. 4. ZnO-catalyzed photooxidation of thiobencarb in commercial rice fields.

It is apparent that a single ZnO treatment can safely reduce thiobencarb levels in sunlit, flooded rice fields through catalyzed photooxidation. However, the present inconsistency of results from large-scale application is troublesome and demands explanation. Further, while ZnO could prove useful in the event of a pesticide spill or accidental overapplication, it cannot provide a license for careless handling or a means for routine removal of pesticide residues from field water.

ACKNOWLEDGMENTS:

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THE COMBINED APPLICATION OF OZONE AND UV IRRADIATION FOR THE TREATMENT OF WATER

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ABSTRACT:

Ozone in combination with ultraviolet light will oxidize compounds which are resistant to ozonation or UV irradiation. Most systems combine the ozone absorption, the ozone reactions and the UV/Ozone treatment of the contaminated water in one step. WEDECO has patented a process which separates these steps in different parts of the unit.

During the first step, ozone is dissolved in post-treated water. Then contaminated water is mixed with the ozonated water. The reaction of ozone alone occurs in a reaction vessel and this is followed by UV irradiation for the production of hydroxyl radicals from the dissolved ozone. The reaction vessel is replaced by an ozone absorption tank when only the radical reaction is required.

The process was tested in the laboratory and then by full scale treatment of biologically treated landfill leachates and contaminated ground water.

The COD and AOX of the above leachates were reduced by more than 90 percent. The chloroform, tri- or tetrachloroethylene in the ground water were mineralized into carbon dioxide and HCl. Capital and operating costs are reported.

INTRODUCTION:

The best method for the treatment of contaminated waters depends upon the selection of the proper combination of treatment processes.

The mild wet oxidation by ozone and its combination with UV irradiation are of growing importance for water treatment besides biological treatment, flocculation, sedimentation, filtration, ion-exchange and reverse osmosis.

This study looked at the use of a two and three step UV and ozone process for the treatment of organically contaminated waters.

METHODS:

A Laboratory Study:

The experiments in the laboratory used the UV and ozone system shown in Figure 1. One to five litres of the test waters were used in the apparatus to determine the quantity of ozone and the rate of removal of COD and AOX from biologically treated and untreated leachate from one municipal landfill and from the biologically treated leachate of another municipal landfill site. A ground water containing trichloroethylene was also studied.

The ozonator produced 5 g/h of ozone from oxygen at a concentration of 100 g/m³.

The UV lamps produced 0.5 watts of UV light at a wavelength of 254 nm.

The experiments were done with oxygen only to determine the rate of stripping of the volatile compounds. A new sample was introduced into the reactor and treated with ozone and UV light until no further oxidation took place.

The concentration of ozone was measured in the production and off gas. The difference is the reacted ozone.

Samples were taken for analysis at time zero, after ozonation and UV/Ozone oxidation.

The ozone concentration was measured by the UV method. The COD was measured by the potassium dichromate method. The AOX was measured by microcolometric detection (Cl, BrI).

Trichloroethylene was measured by gas chromatography using the head space method.

B Bull Scale Field Studies:

B1 Ground water contaminated with halogenated hydrocarbons.

Figure 2 describes the UV/Ozone system for the elimination of chloroform, tri- and tetrachloroethylene in ground water. The contaminated water was pumped through the UV/Ozone reactor. Part of the water stream was removed after the UV reactor by a high pressure pump and forced through an injector and absorption tank to absorb ozone produced from air. The ozone in the off gas was catalytically destroyed. The part stream of ozonated water was mixed with the contaminated water in front of the UV unit. In this unit the reaction takes place between the ozone, UV light and the halogenated hydrocarbons.

A full scale system was studied. This system produced 50 g/h of ozone and 300 watts of UV-C for 10 m³/h of contaminated water. The UV light was produced by a medium pressure mercury lamp.

B2 Landfill Leachates

The flow diagram for the UV/Ozone unit for treating the landfill leachate after an activated sludge plant is shown in Figure 3. Raw water is injected into a stream of recycled treated water. The recycled stream of water absorbs the ozone. The ionic reaction takes place in the two reaction vessels. The radical reactions occur between the ozone, UV light and organic matter in the UV system.

The ozone generator produces 1.5 kg/h of ozone from air. The UV system in the recycled stream of water produces 1000 watts of UV-C from low and medium pressure mercury lamps.

The system was designed for 1.5 to 2.5 m³/h but the flow rate was varied from 0.4 to 2.5 m³/h.

The minimum retention time for the ionic reaction was 1.2 hours.

The ozone generators and the full scale systems were manufactured by WEDECO and housed in a prefabricated container. The typical WEDECO ozonator uses 12 kwh of electricity to produce 1 kg/h of ozone from air at a concentration of 20 g/m³ at a cooling temperature of 10 C (1).

RESULTS OF THE LABORATORY STUDIES:

The results of the oxidation of the trichloroethylene with ozone and UV in combination are shown in Figure 4. Figure 4 also shows the results of stripping with oxygen.

The results of the removal of AOX and COD from the leachate of a landfill site (P) are shown in Figures 5 and 6 respectively. The results of the removal of AOX and COD from this same leachate after biological treatment are shown in Figures 7 and 8 respectively.

The results of the UV/Ozone removal of AOX and COD from a second biologically treated leachate from a landfill site (B) are described in Figures 9 and 10 respectively.

RESULTS OF THE FULL SCALE STUDIES:

Table 1 shows the results of treating the ground water contaminated with halogenated hydrocarbons. Only one percent of the trichloroethylene in the water remained after the treatment process whereas 3.4 percent of the tetrachloroethylene was not destroyed.

Table 2 shows the change in COD and AOX of a biologically treated leachate from a landfill site (B) after treatment with ozone alone and a combination of ozone and UV light.

DISCUSSION:

In the laboratory and field studies the tri- and tetrachloroethylene in the ground water were almost completely mineralized to carbon dioxide and HCl by the combination of UV light and ozone. In both studies there were no detectable by-products in the treated water as determined by gas chromatography. The field study showed that a long reaction time is not required if the proper combination of UV light and ozone is used for the radical reaction.

When the leachate from the landfill sites were treated with the UV/Ozone combination the AOX was quickly reduced to the German limit of 500 ug/l but the COD still remained above the German limit of 200 mg/l. As shown in Figures 6, 8 and 10 to reduce the COD down to the German limit requires a substantial increase in the amount of ozone when the AOX has already reached 500 ug/l. Since the AOX which is the toxic portion of the leachate has been removed the treated leachate can be sent to a biological treatment plant for further processing.

Studies have shown that the partial ozonation of refractory compounds increases their biodegradability. Substantial capital and operating costs can be saved by treating the detoxified waste by a biological process after UV/Ozone.

As shown at landfill site B (Figures 5, 6, 9 and 10) the combination of biological treatment and UV/Ozone is practical whereas UV/Ozone alone was not possible.

CAPITAL AND OPERATING COSTS:

A: The capital and operating costs (Canadian Dollars) for the UV/Ozone system for treating 10 m³/h of ground water contaminated with > 500 ug/l of chlorinated hydrocarbons to < 8 ug/l are shown below. The UV/Ozone system produces 50 g/h of ozone and 300 w/h of UV-C.

1.	Running Costs	: 1 kwh of power costs	\$ 0.17
	Air Drying	: 0.5 kwh =	\$ 0.086
	Ozone Production	: 0.8 kwh =	\$ 0.137
	Ozone Injection	: 1.1 kwh =	\$ 0.188
	UV Light	: 2.0 kwh =	\$ 0.342
	Total	4.4 kwh =	\$ 0.753
	For 1 m ³ of water	0.44 kwh =	\$ 0.075

2. Capital Cost for the UV/Ozone system including the installation and start up
Capital Cost: \$52,500

Interest 6.5% at a 15 year amoratorization period.

Annuity 10.5%

$$\frac{\$2,500 \times 0.105}{12 \times 30 \times 24 \times 10 \text{ m}^3} = \$ 0.064/\text{m}^3$$

3. Supplies and Maintenance \$ 3400/year

$$\frac{\$ 3400}{8,600 \text{ h} \times 10 \text{ m}^3} = \$ 0.039/\text{m}^3$$

4. Total Cost for 1 m³ of water
 - Running Costs : \$ 0.075
 - Capital Costs : \$ 0.064
 - Supplies & Maintenance: \$ 0.039
 - Total Costs/m³ : \$ 0.178

B. The capital and operating costs for a UV/Ozone system which treats 8 m³/h of biologically treated landfill leachate are presented. The COD is reduced from 900 mg/l to < 100 mg/l and the AOX from 900 ug/l to < 100 ug/l. The UV/Ozone system uses oxygen recycling for ozone production at the rate of 12 kg/h at 100 g/m³. A medium pressure mercury lamp produces 3 kw of UV-C.

1.
 - Running Costs : 1 kwh of power costs \$ 0.17
 - Ozone Production : 72.0 kwh = \$12.33
 - Gas Preparation : 1.2 kwh = \$ 0.20
 - Ozone Injection : 37 kwh = \$ 6.33
 - Water Pumps : 2.0 kwh = \$ 0.34
 - Cooling : 30.0 kwh = \$ 5.14
 - UV Light : 20.0 kwh = \$ 3.42
 - Oxygen (Volume = 9 m³/h at \$0.56/m³) = \$ 5.05
 - Total Running Costs = \$32.81
 - Running costs for treating 1 m³/h of contaminated water
 - \$32.81 = \$ 4.10/m³
 - 8 m³

2. Capital Cost for UV/Ozone system including installation and start-up.
 Capital Cost: \$ 1,164,400
 Interest at 6.5% per year with an amortization period of 10 years.
 Annuity 14%

$$\frac{\$1,164,400 \times 0.14}{12 \times 30 \times 24 \times 8 \text{ m}^3} = \$ 2.36/\text{m}^3$$

3. Supplies and maintenance

$$\frac{\$ 1,164,400 \times 0.01}{12 \times 30 \times 24 \times 8 \text{ m}^3} = \$ 0.168/\text{m}^3$$

4. Total Cost per m³ of treated water
 - Running Cost = \$ 4.10/m³
 - Capital Cost = \$ 2.36/m³
 - Supplies and Maintenance = \$ 0.168/m³
 - Total Cost = \$ 6.63/m³

CONCLUSIONS:

Alone or in combination with other processes UV/Ozone is an economical and environmentally safe alternative for the treatment of contaminated water. An example of a WEDECO UV/Ozone unit is shown in Figure 11.

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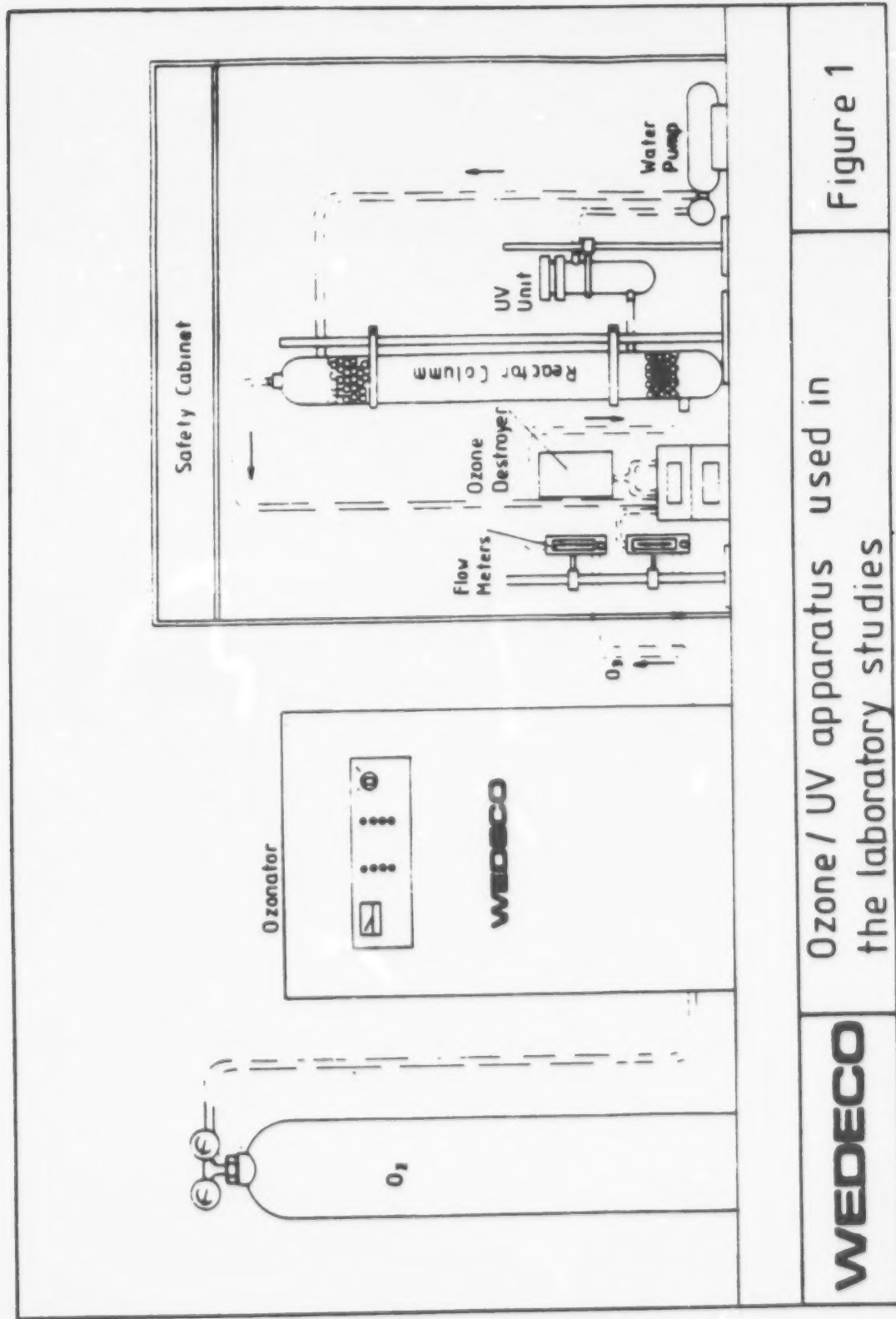
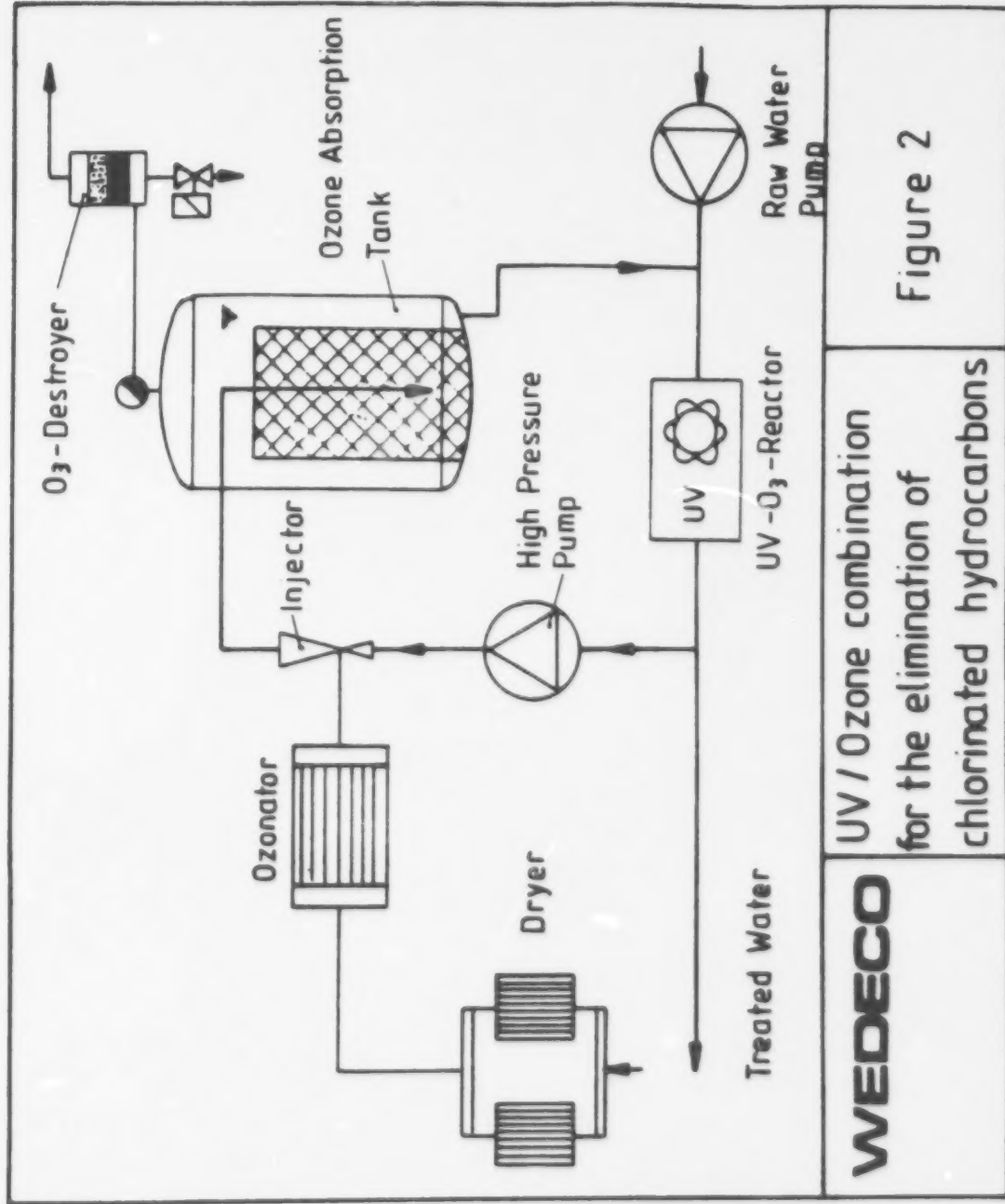


Figure 1

Ozone / UV apparatus used in the laboratory studies

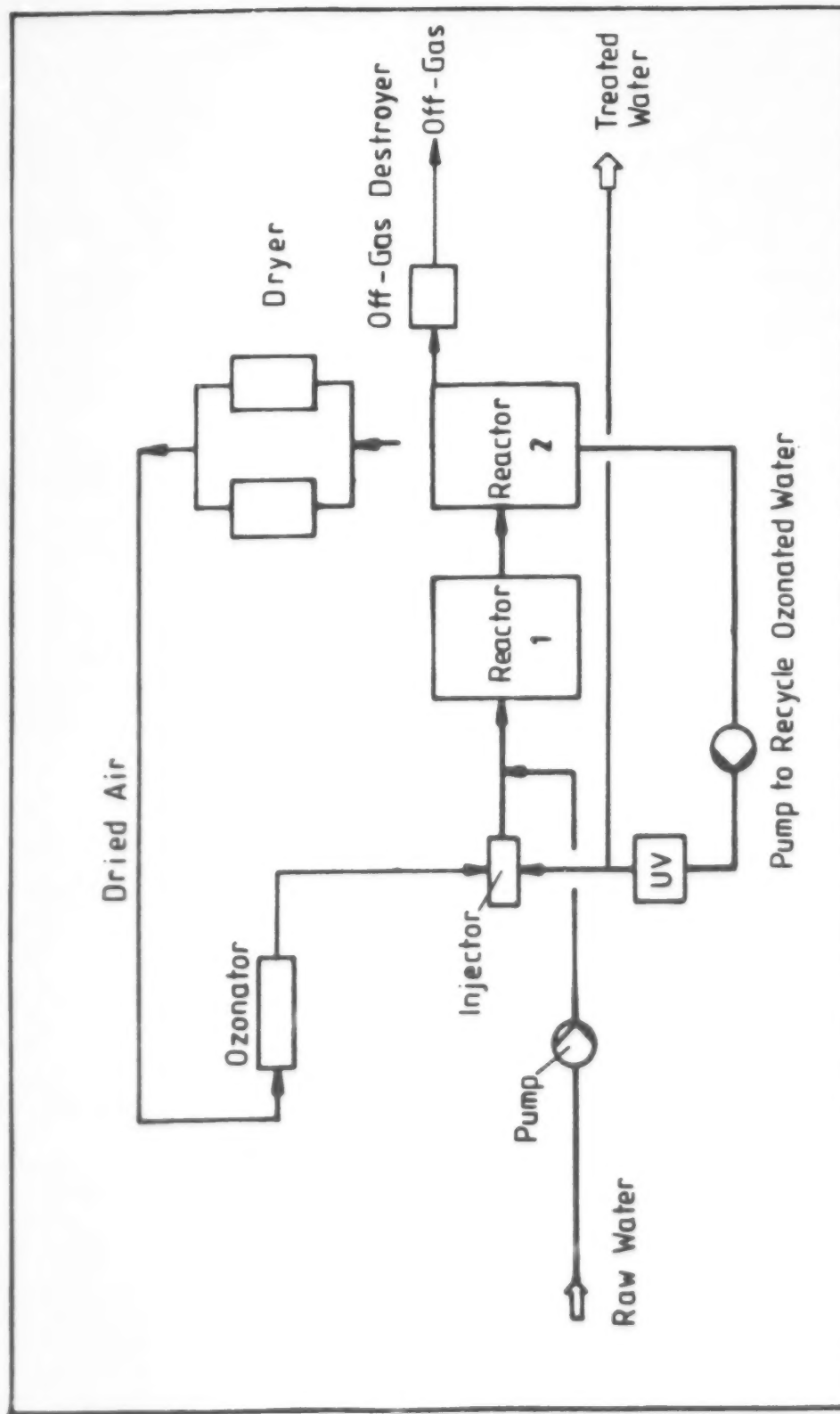
WEDECO



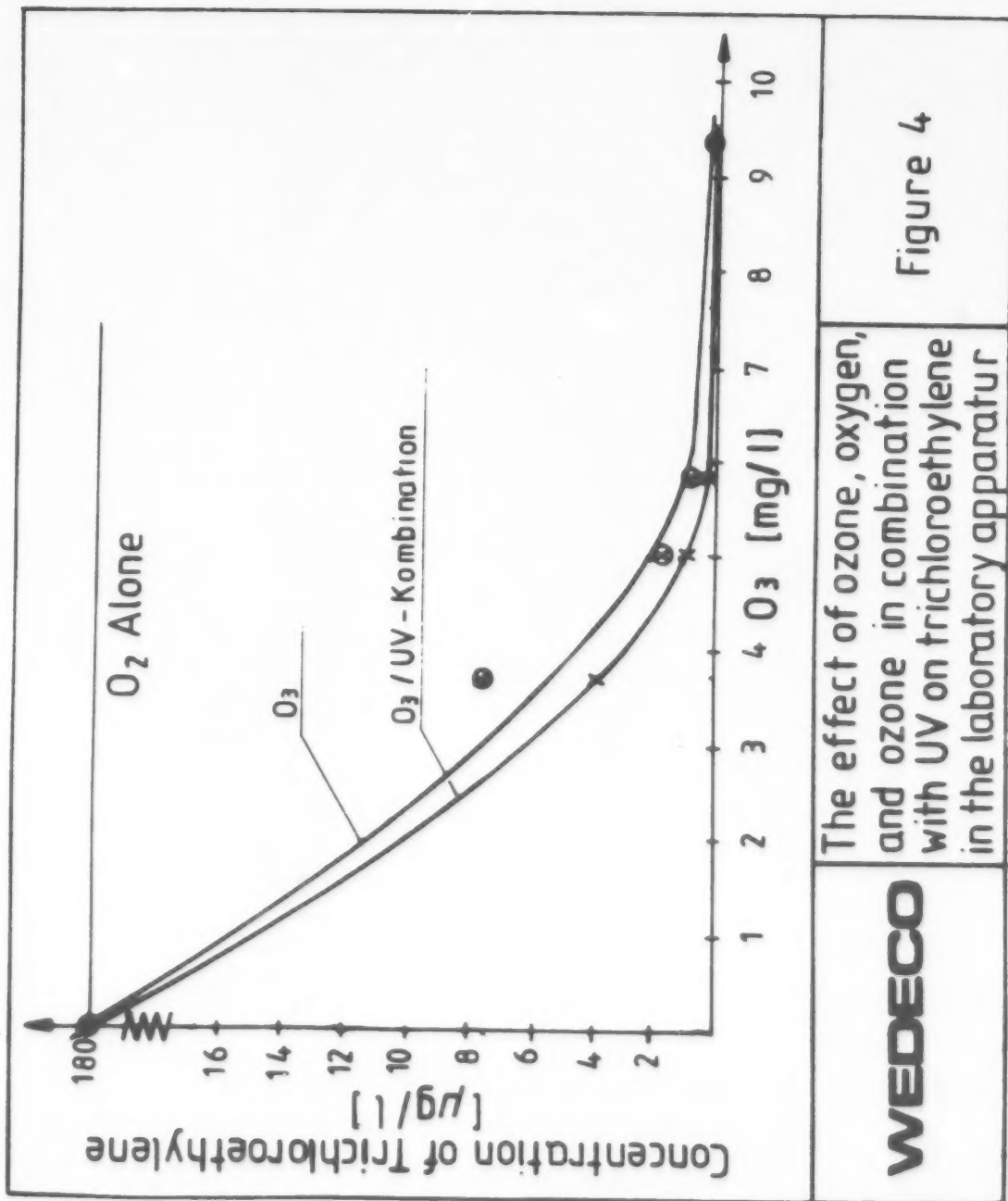
WEDECO

UV / Ozone combination
for the elimination of
chlorinated hydrocarbons

Figure 2



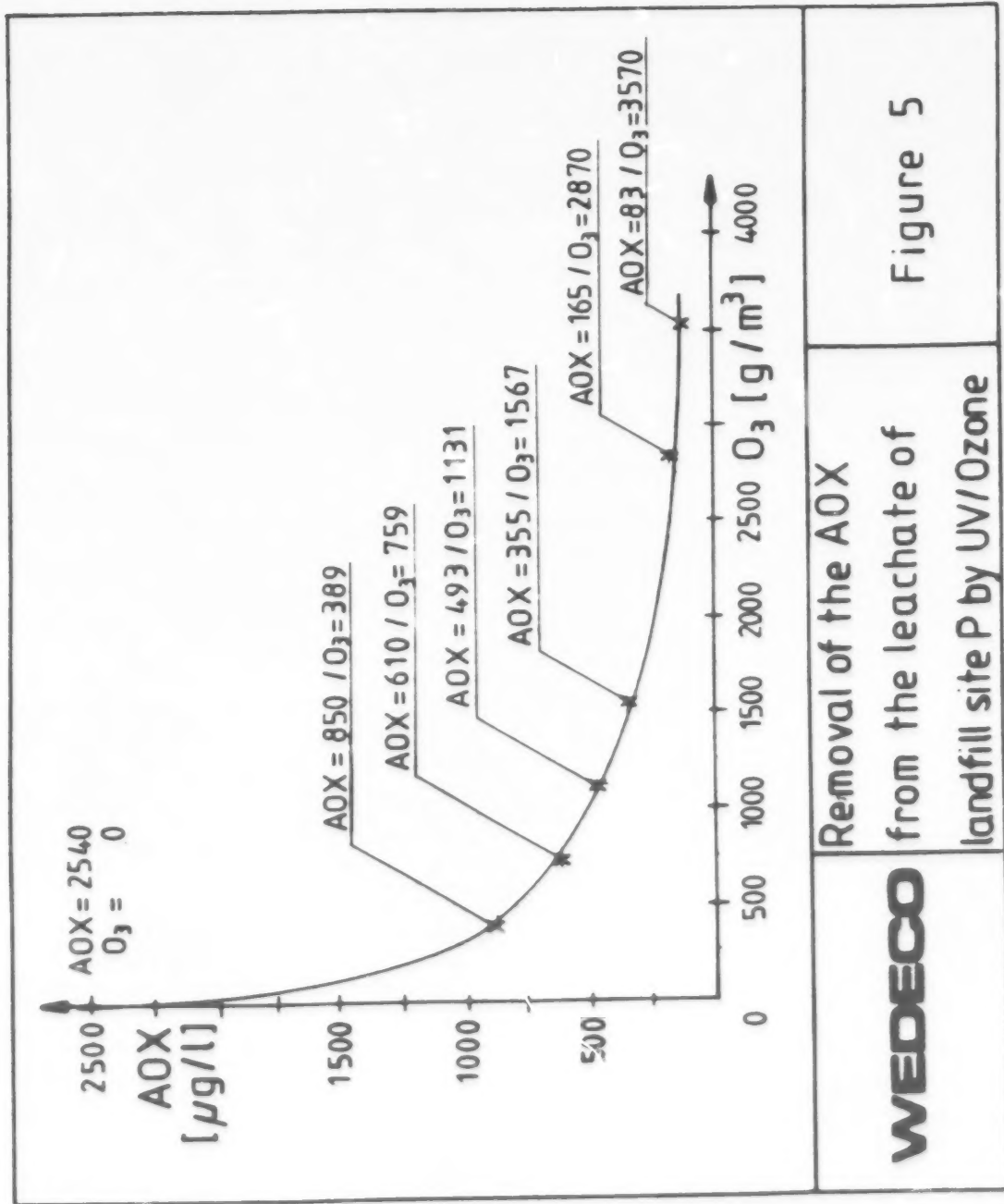
WEDECO	UV / Ozone Unit for Biologically Treated Landfill Leachate	Figure 3
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WEDECO

The effect of ozone, oxygen, and ozone in combination with UV on trichloroethylene in the laboratory apparatus

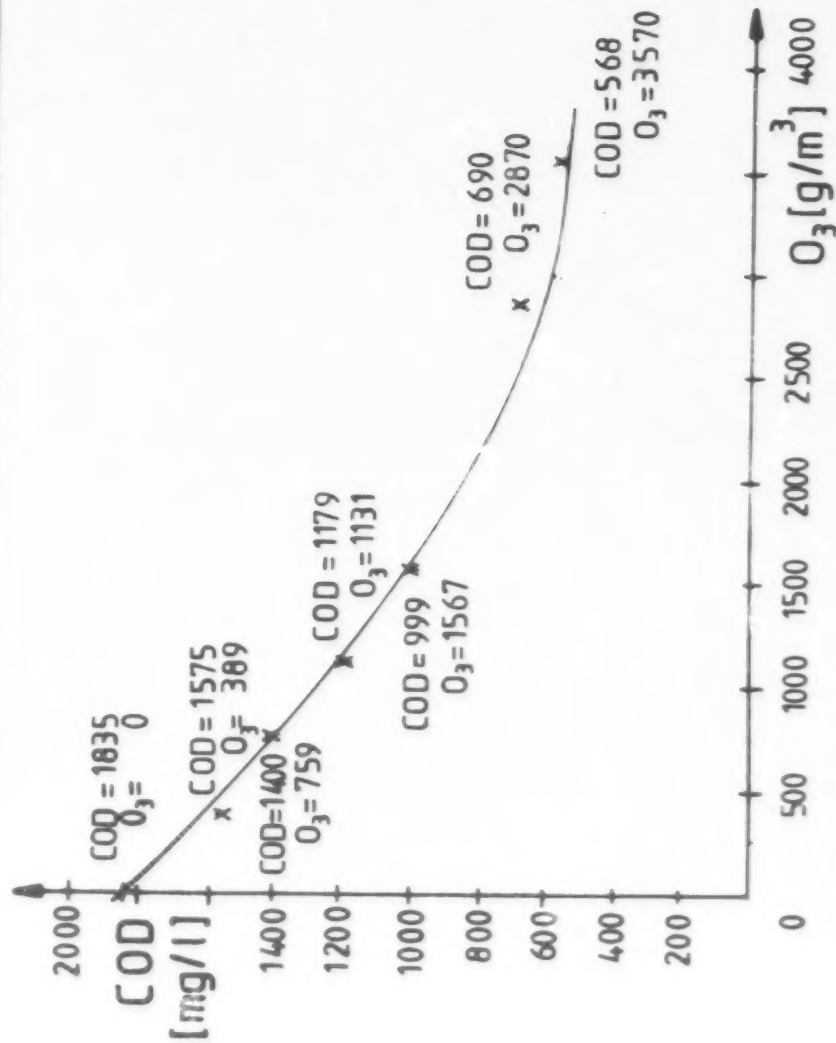
Figure 4



WEDECO

Removal of the AOX
from the leachate of
landfill site P by UV/Ozone

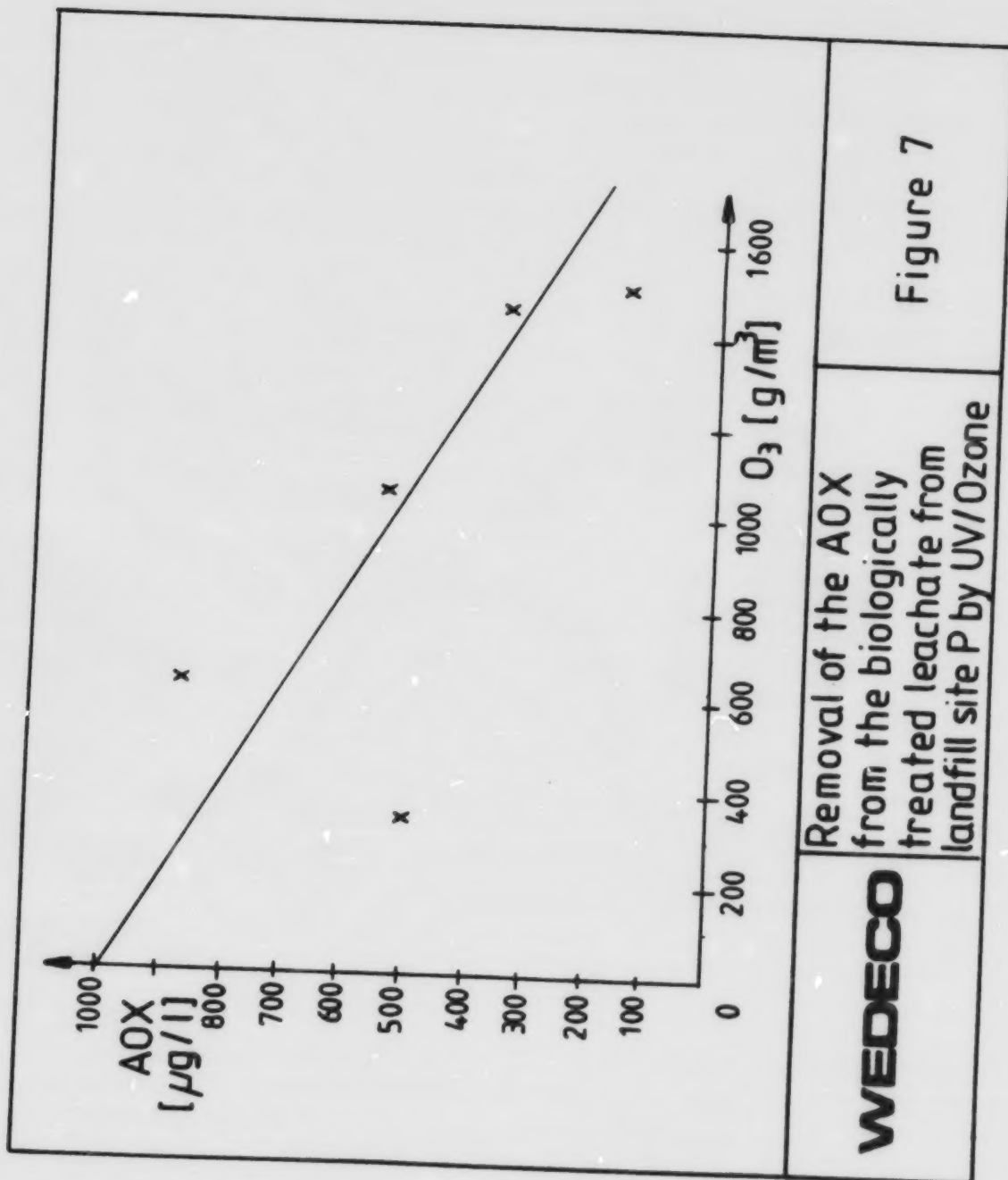
Figure 5

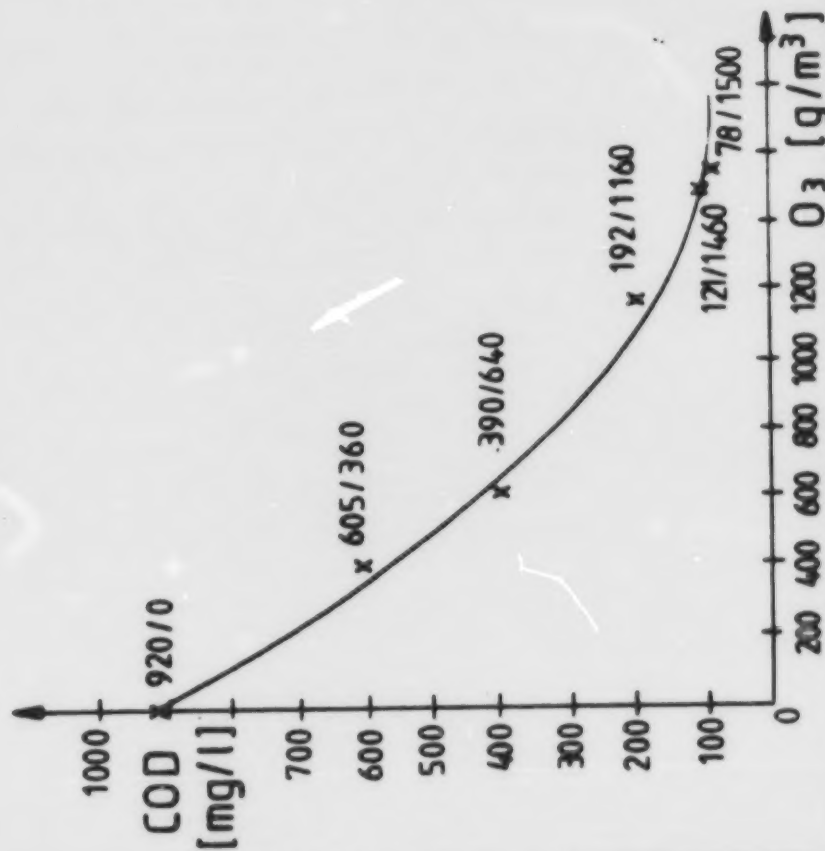


WEDECO

Removal of the COD
from the leachate of
landfill site P by UV/Ozone

Figure 6

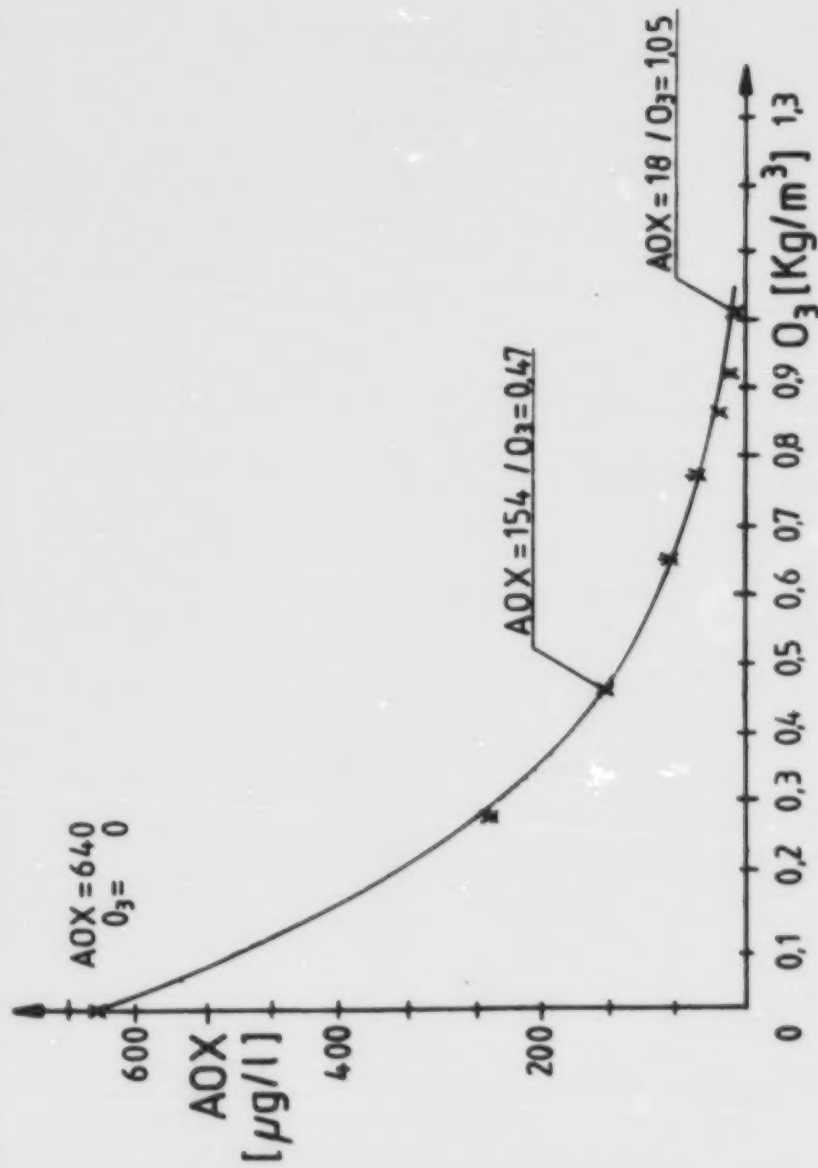




WEDDO

Removal of the COD
from the biologically
treated leachate from
landfill site P by UV/Ozone

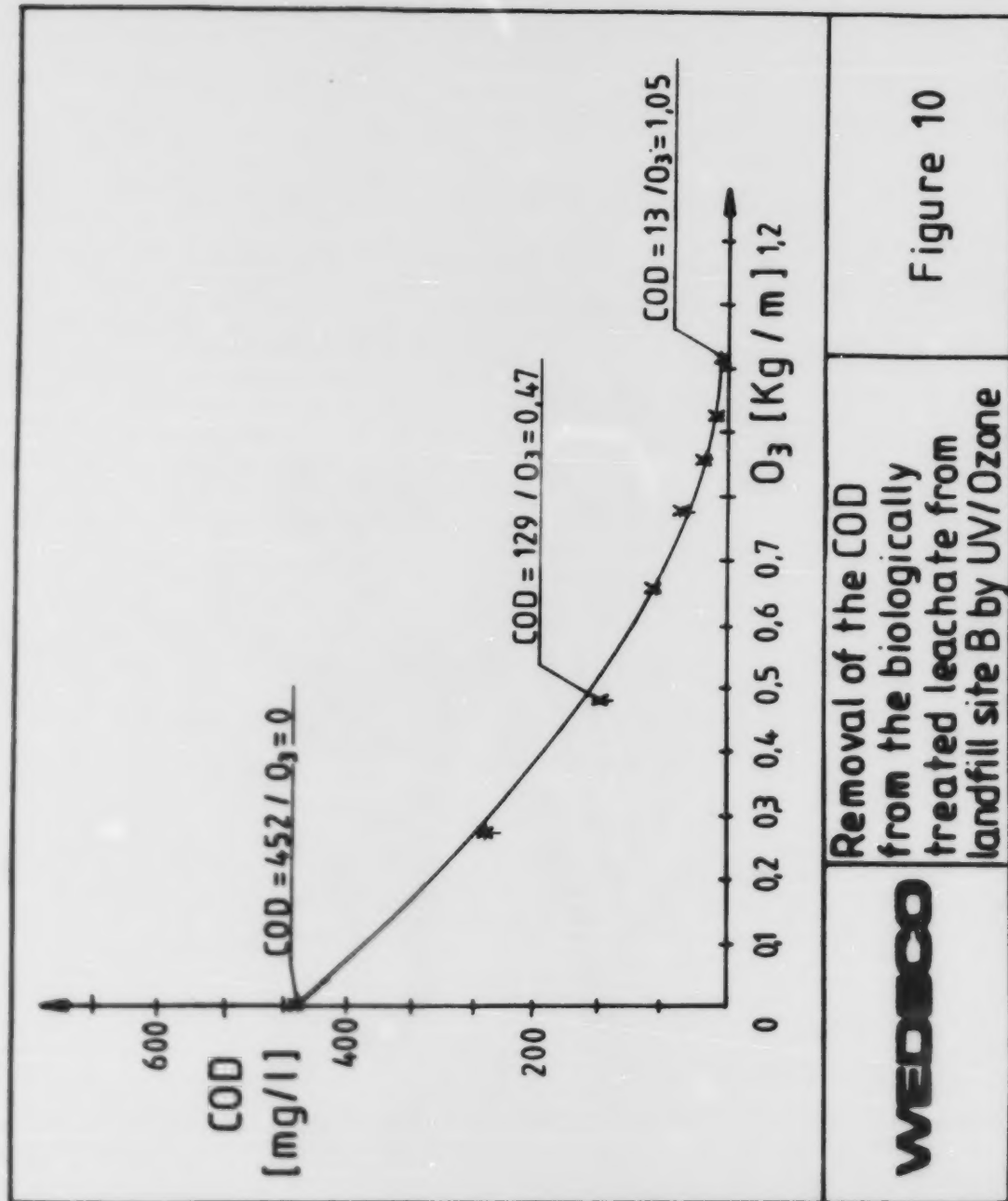
Figure 8



Removal of the AOX
from the biologically
treated leachate from
landfill site B by UV/Ozone

WEDECO

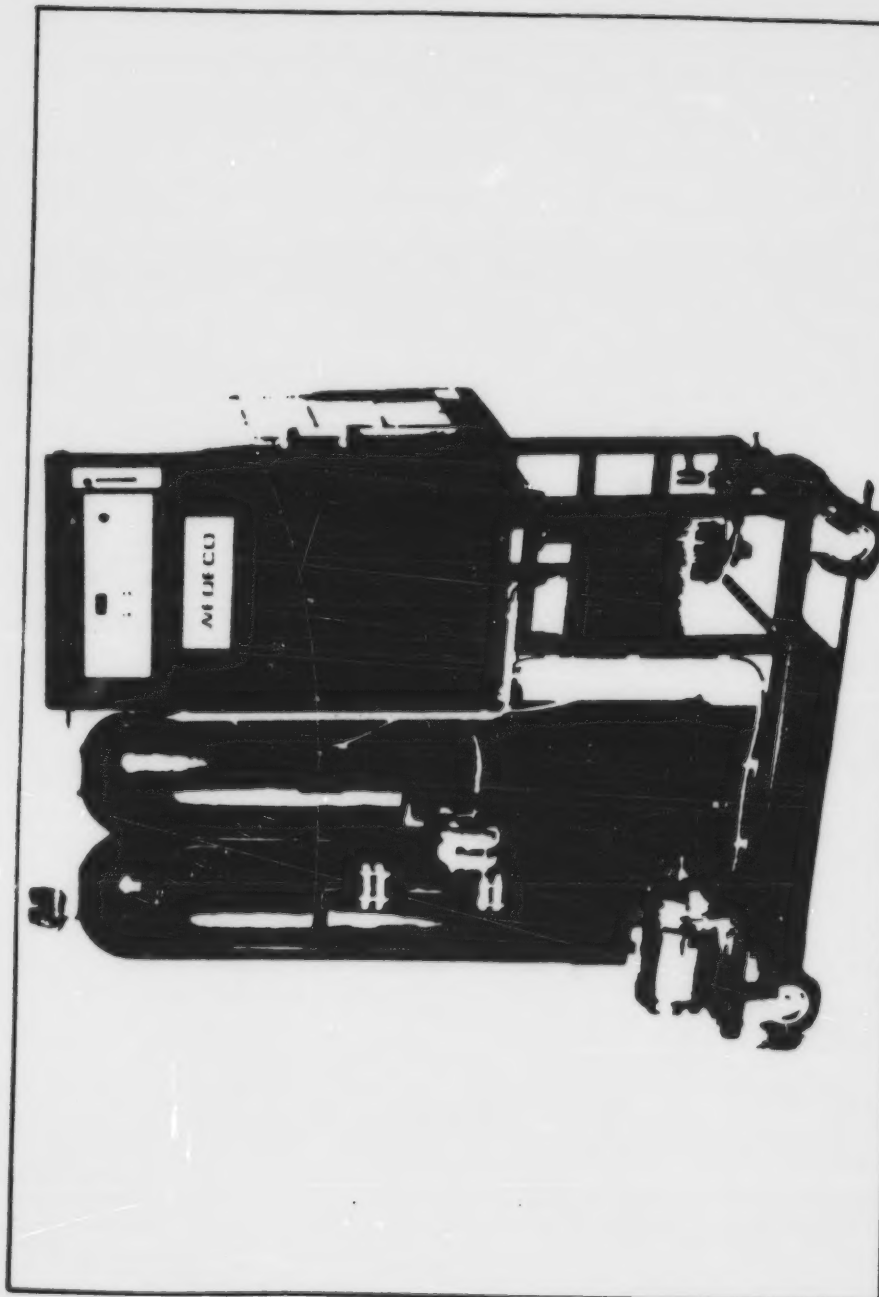
Figure 9



Removal of the COD
from the biologically
treated leachate from
landfill site B by UV/Ozone

WEDICO

Figure 10



UV/Ozone Unit for
treating AOX and COD
in Water Type SEA 35/UV

WEDECO

Figure 11

Parameter	Raw Water µg/L	Treated Water UV/O ₃ µg/L
Dichloromethane	< 10	< 10
1,1,1 Trichloromethane	0,45	0,26
Trichloroethylene	> 330	3,2
Tetrachloroethylene	> 160	5,5
Carbontetrachloride	< 0,1	< 0,1
Dibromomethane	< 0,2	< 0,2
Chloroform	0,9	< 0,2
Bromodichloromethane	< 0,2	< 0,2
Dibromochloromethane	< 0,2	< 0,2
Bromoform	< 0,2	< 0,2
WEDECO	Removal of halogenated hydrocarbons from ground water by UV/O ₃ (Water Flow Rate = 10 m ³ /h, 50g/h O ₃ and 300 W/h of UV-C)	
		Table 1

Parameter	After Biological Treatment	After Treatment with O ₃ or UV/O ₃
COD	600 mg/l	O ₃ 140 mg/l UV/O ₃ 105 mg/l
AOX	500 µg/l	130 µg/l 98 µg/l
WEDECO	Results of the treatment of leachate from a landfill site (B) by a biological process and treatment of this biological leachate by O ₃ or UV/O ₃ (Water Flow Rate = 1,5 m ³ /h, 1.2 Kg/h O ₃ , 1 Kw/h of UV-C)	
	Table 2	

QUANTUM YIELDS FOR ALCOHOL OXIDATION PHOTOCATALYZED BY TiO_2

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ABSTRACT:

Relative initial quantum yields (Φ'_0) of two alcohols (1-propanol and methanol) as well as an aldehyde (propanal) were determined employing a commercial photoreactor (stationary TiO_2). These yields were compared to those measured with illuminated TiO_2 dispersions in the presence of 1-propanol. A quantum yield, $\Phi'_0 > 1$ was obtained for 1-propanol in the photoreactor.

The high quantum yield value for the photoreactor was attributed to the high coverage of occupied active sites and more efficient competition of substrate oxidation with electron/hole recombination, over the low surface area of the stationary TiO_2 , in contrast to the higher surface area dispersion.

The inhibition of the reaction with build up of products was characteristic of reactant/product competition for the available sites on the photocatalyst. Methanol proved to be less rapidly oxidized than 1-propanol or propanal.

INTRODUCTION:

In the past decade or so, semiconductor photocatalysis has been extensively studied for the degradation of organic contaminants in water [1-8]. This technology has evolved to the point of becoming a potential process for wastewater treatment, since it has been demonstrated to render most toxic pollutants virtually harmless [1-11].

Titanium dioxide has been favoured as a photocatalyst for treating aqueous wastes, because of the strongly oxidizing potential of its valence band holes and also for its photo-stability. Many of the studies carried out with TiO_2 have used small-scale aqueous suspension systems [1-5,7,10]. These systems, however, are impractical for large-scale applications since the particle size of TiO_2 is often less than a few micrometers. A more viable approach would be to have the photocatalyst bound to an inert stationary support, where the semiconductor, where the semiconductor would still retain its chemical and physical characteristics.

The photocatalyzed process is achieved by the illumination of TiO_2 with light energy greater than its band-gap energy ($\leq 388 \text{ nm}$) in order to create electronic excitation within the solid

[18]. The electron is excited to the conduction band, leaving a vacancy ("hole") in the valence band. The photo-produced electron/hole pairs may migrate to the surface of the semiconductor.

The valence-band holes and conduction electrons give rise to reduction or oxidation processes with adsorbed species, surface groups, or with the bulk semiconductor itself. Hydroxyl radicals have been considered as the reactive species involved in the photocatalytic degradation of many contaminants.

In the absence of suitable hole or electron scavengers at the surface, recombination will occur (within a few nanoseconds) and the energy absorbed will dissipate as heat [12,13]. However, it has also been shown that interfacial charge transfer can occur in less than 10ps [19].

The objective of this study is to evaluate a central question concerning practical reactors employing stationary TiO_2 . Is the efficiency controlled by inherent limits imposed by efficient electron-hole recombination in TiO_2 which recommends modification of the composition of the oxide? Or, alternatively, is TiO_2 sufficiently reactive for sorption, desorption, and mass transport to control efficiency? For this purpose, we focus on readily oxidizable substrates, alcohols. A subsidiary goal of the work is to compare the prototype reactor to the sort of dispersion experiments that are commonly examined in the literature.

EXPERIMENTAL:

Chemicals:

Methanol spectroscopic grade (ACP), 1-propanol anhydrous 99+%, propionaldehyde 99+%, 1,10-phenanthroline 99+% and propanoic acid 99+% gold label were purchased from Aldrich. P-25 titanium dioxide was obtained from Degussa. Ferric chloride (J.T. Baker Co.) and potassium oxalate (Fisher) were laboratory grade. All chemicals were employed without further purification. Doubly deionized distilled water was used throughout this study.

Instruments:

Quantitative analysis of reactant and product concentrations were monitored with a Perkin-Elmer Sigma 2 gas chromatograph interfaced with a Sigma 10 data station. The instrument was equipped with a flame ionization detector and a Chromosorb 101 packed column (Chromatographic Specialties Inc.). The operating conditions were: column temperature

(isothermal) 130°C; injector temperature 180°C; detector temperature 200°C; and the carrier gas was prepurified nitrogen with a flow rate of 30mL/min.

Products formed were analyzed with a Hewlett Packard GC/MSD (5890 gas chromatograph/5970 mass selective detector) interfaced with a 9000/216 data station. The analysis were conducted by temperature programming: 70°C initial and adjusted to 1°C/min., with a final temperature of 120°C. The injection port was set to 150°C and the detector zone at 250°C. The column employed was a Hewlett Packard pona capillary, crossed linked methyl silicone gum (50m x 0.2m x 0.5µm film thickness). The flow rate of the prepurified helium was 8mL per min. The MSD was set to scan 20 to 500amu.

Photocatalytic Systems:

Two systems were employed in this study; system I, consisting of a prototype commercial photoreactor (courtesy of Nulite [14]) (Fig.1a) and system II, a TiO₂ dispersion (Fig.1b).

The photoreactor was constructed from a stainless steel jacket (34cm length x 2.3cm inner wall radius), a lamp and a photocatalytic mesh. The lamp (Phillips Electronics Ltd., "TL" 44 D25/09N) emits radiation in the 320-390nm range with a peak at 350nm. The lamp was arranged coaxially within the jacket and encircling it was a fibreglass mesh coated with a firmly bonded layer of anatase titanium dioxide (patented process [14]). The radiant intensity inside the reactor was determined by potassium ferrioxalate actinometry (via continuous flow) following the Hatchard and Parker technique outlined by Gordon and Ford [15]. The available intensity was found to be 1.3×10^{18} photons per second with bare mesh and TiO₂ sleeve. This value represents the maximum possible photon absorption rate for the anchored photocatalyst during photoreaction.

The bound titanium dioxide layer was found to have a Brunauer-Emmett-Teller (BET) surface area of $8.20 \pm 1.48\text{m}^2/\text{g}$ in comparison to the bare fibreglass mesh $6.56 \pm 0.78\text{m}^2/\text{g}$.

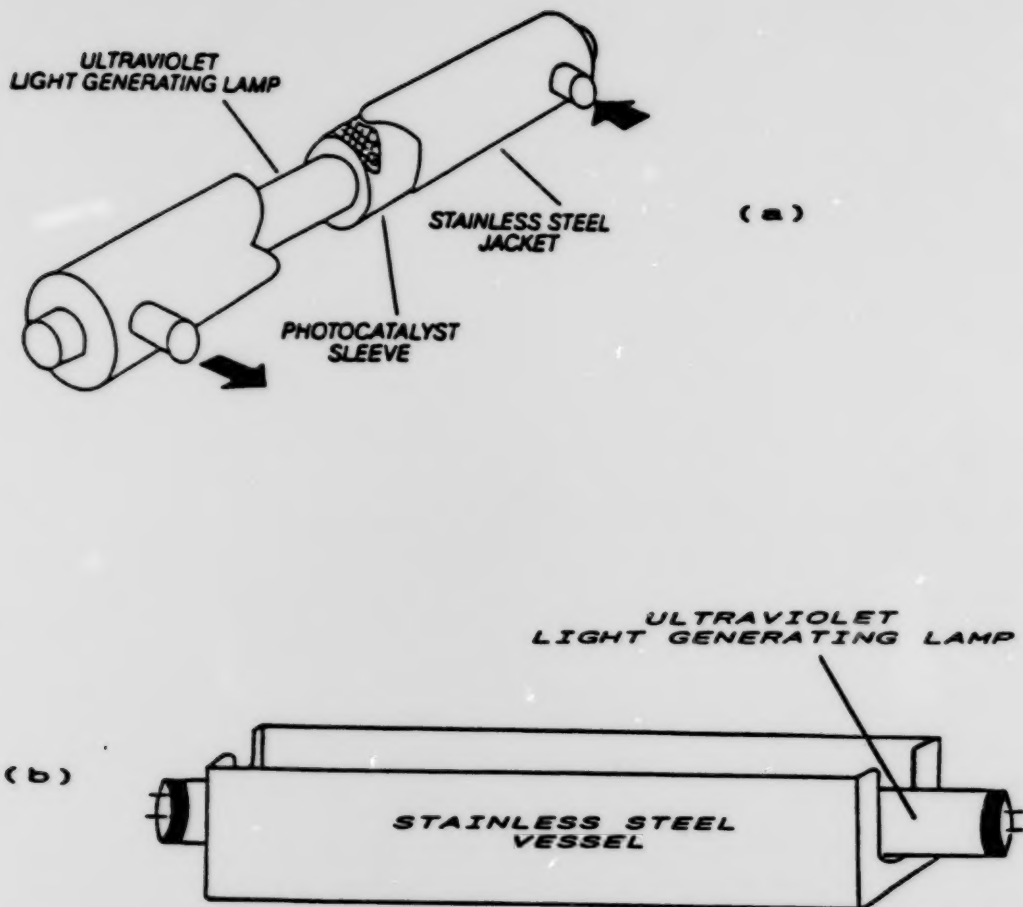


FIGURE 1 An illustration of the experimental systems employed (a) System I: a commercial photoreactor, TiO_2 fixed on a stationary support (diagram courtesy of Nulite) (b) System II: a TiO_2 dispersion.

The total volume of solution circulated in the reactor was 750mL, with a dead volume of 410mL. The liquid was recycled with an oscillating pump (Gormann-Rupp Industries Inc.) with a flow rate of 150mL/min into a one litre reservoir. The open pore and configuration of the sleeve in the reactor creates a turbulent mixing that ensures contact between reactants and the photocatalyst. A magnetic stirring bar was placed in the reservoir to assure proper mixing and aeration, in addition the outflow from the reactor was located a few centimetres above the surface of the bulk solution. Materials in contact with the solution were stainless steel, polypropylene (pump valve housings), glass and tygon tubing.

Stock solutions were prepared in 2L volumetric flasks and were employed for dark

experiments and photocatalytic reactions.

Sampling was carried out by removing 1.00mL aliquots at different time intervals. These aliquots were then placed in 2mL sealed vials and refrigerated for later analysis. After every run the system was flushed with five litres of water with the lamp turned on.

In system II (TiO_2 dispersions), the reaction vessel consisted of a stainless steel container (2.0cm height x 4.5cm width x 38.0cm length) where the lamp (Phillips Electronics Ltd., "TL" 44 D25/09N) was fitted horizontally onto two grooves at the ends of the vessel. The lamp intensity in this static system was found to be 1.6×10^{18} quanta per second in the absence of the photocatalyst.

The total volume used throughout the experiment was 250mL. The bulk solution was kept thoroughly mixed by three stirring bars at different locations along the vessel.

Seventy-five milligrams of TiO_2 was employed as a dispersion during this study. The colloidal photocatalyst was verified to have a (BET) surface area of $55.7 \pm 0.5 \text{ m}^2/\text{g}$. Sampling of solutions containing these fine particles of TiO_2 was accomplished by removing 2.00mL aliquots at separate time intervals and centrifuging (International Equipment Co.) them for 20 minutes at 4750 rpm. A portion of the centrifuged liquid was withdrawn with a pasteur pipette and transferred in 2mL sealed vials and refrigerated for later analysis.

In both system I and II, blank experiments were conducted to monitor for the possibility of substrate loss and susceptibility to oxidation by the atmosphere. These results were then subtracted from the photocatalysis experiments. In addition, the bulk solution was monitored for pH and temperature changes.

The lamps in both setups were warmed up for 10 min. prior to each trial.

RESULTS AND DISCUSSION:

The quantum yield for a reaction is defined as the number of moles reaction per mole of photons (einsteins) absorbed. The quantum yield is the essential parameter for addressing the central question of this study, the origins of limits on efficiency of photocatalysts. Unfortunately, it is difficult to measure the light absorbed by the catalyst reliably. In this paper we discuss a parameter Φ' which is a quantum yield based on the assumption that light intensities measured by the ferrioxalate actinometry correspond to intensities absorbed. The weak dependence of observed intensity on actinometer concentration in the commercial

photoreactor suggests that this approximation is excellent. Relative values of Φ' given below remain significant in any case since the variations examined do not affect the efficiency of light absorption by TiO_2 .

$$\Phi'_0 = [C_p/V * t]/I \quad (1)$$

$$\Phi'_0 \text{ dis.} = [(C_0 - C_i)/(V * t)]/I \quad (2)$$

Φ'_0 : quantum yield of product formed

$\Phi'_0 \text{ dis.}$: quantum yield of the sum of products formed or the disappearance of the reactant

C_p : moles of individual product formed (1°, 2°, 3°...etc.)

C_0 : initial moles of reactant

C_i : moles of reactant remaining in the i^{th} irradiated sample

I : intensity, einsteins of light absorbed by reactant per (volume * time)

V : volume

t : time

The systems were found to differ in lamp intensity, although the lamps employed were the same manufactures model. When the lamps were interchanged similar light intensities were observed. This would suggest the design of the reactors give different dead volumes. Moreover, the presence of the photocatalyst material in either systems may scatter some of the incoming light, this may be an important factor in system II, especially since the actinometry experiments were run in the absence of colloidal TiO_2 . However in system I, no appreciable difference was observed for the ferrioxalate actinometer in the absence or presence of the bound TiO_2 mesh.

In system I several experiments involving methanol, 1-propanol and propanal were performed separately with increasing concentrations, while in system II only 1-propanol was investigated. Both TiO_2 dispersions and the photoreactor consisted of open systems (solutions exposed to the atmosphere). Prior to photocatalysis, blank runs (illumination with no photocatalyst) were conducted with each reactant, since none of these compounds absorb light above 300nm, any change in concentration would be due to loss or air oxidation. The substrates were analyzed for the later possibility by GC/MSD, and only propanal was found to be oxidized to propanoic acid under these circumstances. Significant losses were observed for system II under blank conditions, this confined the investigation to 1-propanol, since it was also possible to monitor its oxidation product. All photocatalysis experiments were corrected for the blank runs.

Reaction temperatures were monitored throughout this study, and were found not to exceed 30°C for both systems. The contribution of thermal decomposition proved to be insignificant, in an experiment in which a 0.062M 1-propanol solution (in the presence of TiO_2) was held at 35°C for 90 minutes. No products were detected. It has been documented, that solution temperatures have an effect on the efficiency of the photocatalyst [16,17].

The pH was also monitored (initial pH=5) but no significant change was observed.

In both setups, the TiO_2 photocatalyst was saturated with solutions containing high reactant concentrations so as to obtain a maximum rate of conversion (Φ_0 dis.). Primary quantum yields were attempted for all three compounds, only 1-propanol yielded a quantifiable product (propanal). The photocatalytic oxidation of 1-propanol is shown in figures 2 and 3, for both systems. A 0.062M solution of 1-propanol was illuminated for a period of 70 minutes in the photoreactor (Fig.2) while a 0.10M solution was irradiated for 60 minutes in the presence of a TiO_2 dispersion (Fig.3).

Measuring the change in the propanol concentration and subtracting propanal, yielded a secondary product (2°). This secondary product may constitute a sum of products, except propanal, formed. To confirm this assumption, a qualitative investigation was performed by GC/MSD. This revealed the presence of propanoic acid in the 2° product. Nevertheless it would be erroneous to assume the 2° product to be solely composed of propanoic acid. It may include all stages of oxidation to CO_2 .

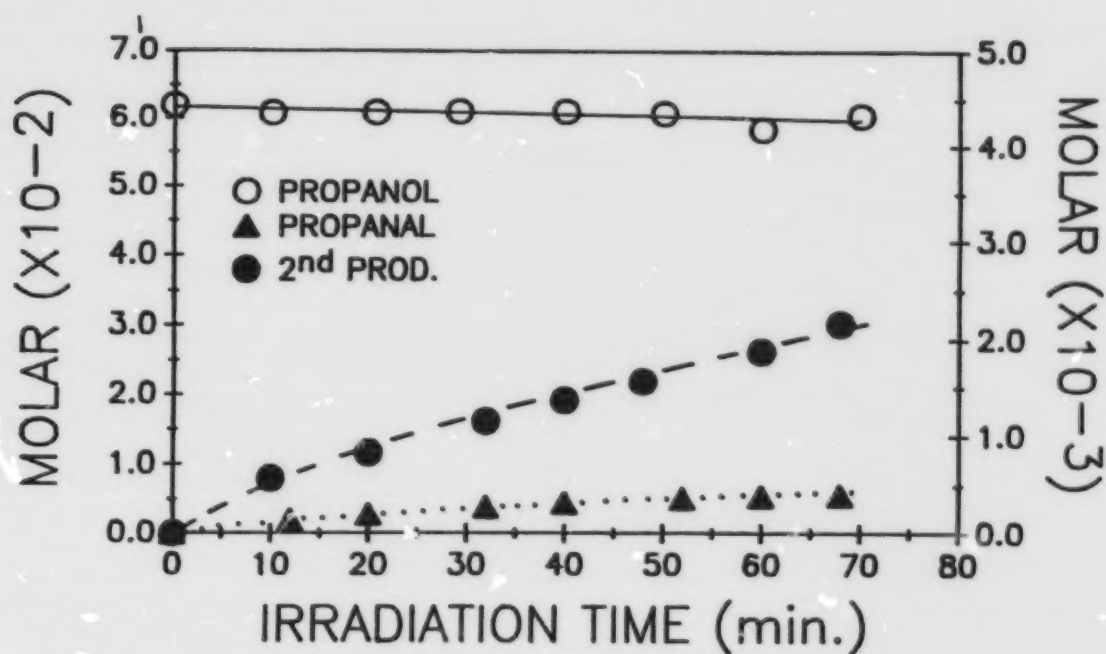


Figure 2 Photocatalysis of 0.062M 1-propanol (o) employing a commercial photoreactor. The concentrations of (▲) propanal and (●) the secondary product formed are represented along the right vertical axis.

Both propanal and secondary product were produced significantly faster in system II than system I. An explanation for this, lies with the surface coverage of TiO_2 on the stationary support (system I). Its surface area ($8.20 \pm 1.48 \text{ m}^2/\text{g}$) would suggest smooth uniform coverage over the fibreglass mesh ($6.56 \pm 0.78 \text{ m}^2/\text{g}$) in contrast to the high surface area found for dispersions ($55.7 \pm 0.5 \text{ m}^2/\text{g}$). This also implies that the dispersion should have a greater number of active sites for substrate adsorption and reaction than the fixed photocatalyst, this was notice in the saturation of the photocatalyst in the presence of propanol in figure 2. Having all the active sites on the photocatalyst occupied by the alcohol would aid in the determination of limiting quantum yield. This is illustrated in figures 4 and 5 where two separate solutions differing in 1-propanol concentrations were illuminated in the presence of TiO_2 in their respective systems.

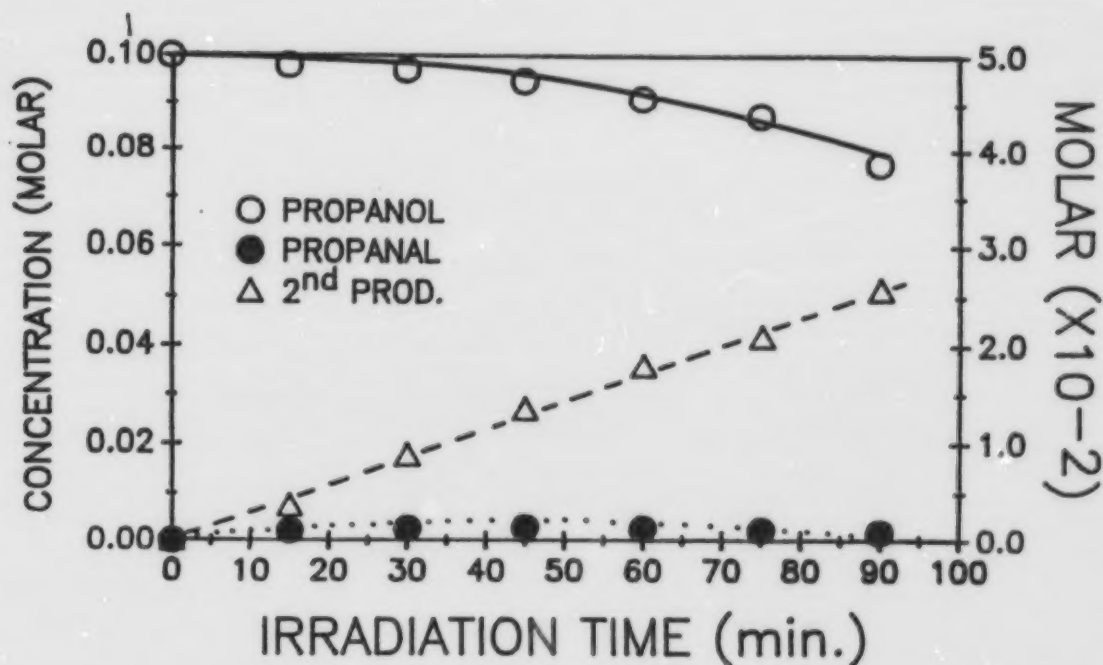


Figure 3 System II: irradiation of 0.10M 1-propanol (o). Propanal (●) and secondary product (△) are represented on the right vertical axis ($\times 10^{-2}$).

We see that the relative quantum yield fall with continuing reaction, more steeply in system I. Extrapolation to $t=0$, however, gives a value of $\Phi'_{\text{p}} > 1$ in the reactor but not on the dispersion (Fig.5). This can be understood by recognizing that saturation of active sites is more easily achieved in the reactor than on the high surface dispersion. The steeper time dependence is similarly explained. With a small number of sites, product competition inhibits the reaction of propanol at an earlier point.

The limiting quantum yield greater than one for 1-propanol answers one of the main questions this study was designed to address. The presence of an oxidizable substrate at high coverage on the TiO_2 leads to the efficient competition with the hole/electron recombination. The main factor lowering the quantum yield in these experiments appears to be product build up. Thus, the key factor determining efficiency is the inter-relation of adsorption, secondary oxidation rate, and product desorption.

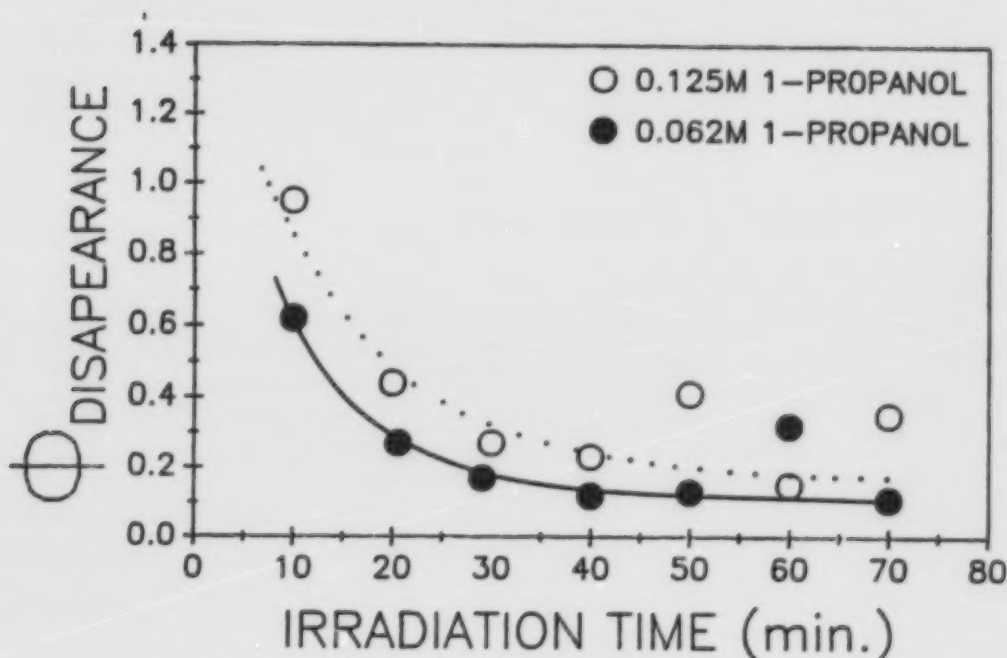


Figure 4 Photoreactor: quantum yields of disappearance (Φ_{dis}) of 1-propanol at different concentrations as a function of irradiation time: 0.125M (o) and 0.062M (●) 1-propanol.

The TiO_2 dispersion in figure 5, displays a moderate decay in the quantum yield of 0.10M 1-propanol in comparison to the quasi linear curve of 0.01M 1-propanol. This tendency is indicative of the availability of sites on the photocatalyst to consume the products generated.

This will tend to reduce the build up of products which might curb the consumption of the propanol, as seen in figure 4. However, increasing coverage on the dispersion will lead to a behaviour similar to that demonstrated in figure 4.

The net production up of primary product, 1-propanol, is illustrated in figures 6 and 7 for both systems.

Unlike system I, the dispersion shows the propanol quantum yield decreases almost linearly in comparison to what was observed for the photoreactor. The decrease is not to be attributed to the shortage of substrate to form propanol but how easily oxidizable propanol is. When a steady state is reached, the net yield of propanol will be zero. The low net Φ_p for propanol production compared to propanol consumption implies that propanol is retained on the surface

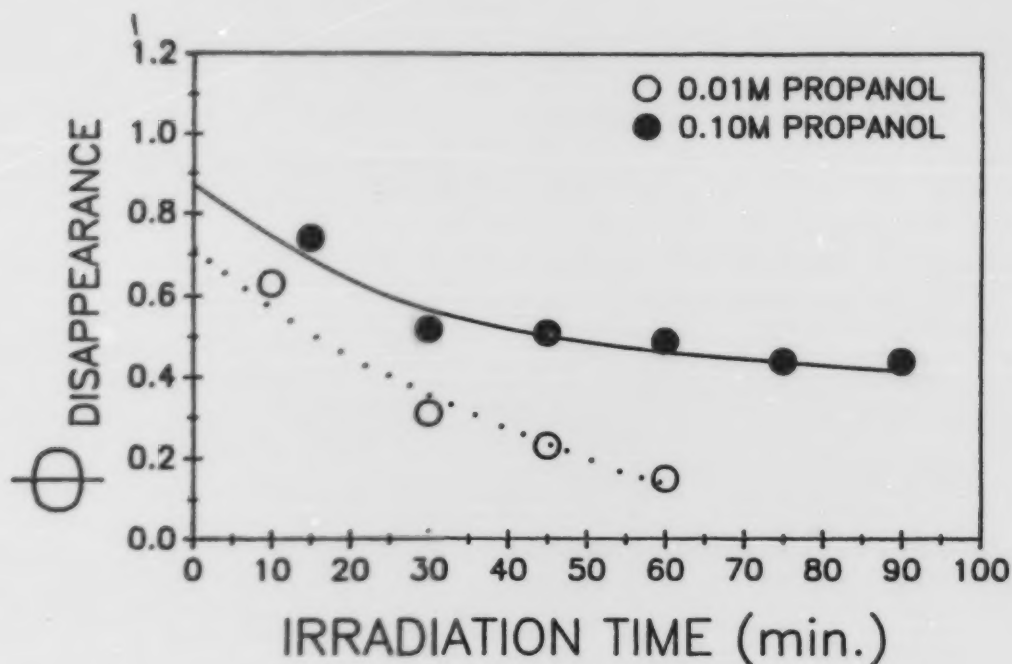


Figure 5 The quantum yields of disappearance (Φ_{dis}) for two concentrations of 1-propanol in the presence of an illuminated TiO_2 dispersion: 0.01M (o) and 0.10M 1-propanol (●).

of the photocatalyst and efficiently oxidized in competition with its desorption into solution. The decrease in the propanal quantum yields in figure 7 reflects the appearance of a steady state, where the propanal is being consumed at the same rate as its production (Fig.3).

A separate experiment was conducted to study the behaviour of the primary product (propanal) employing system I (Fig.8). The lower Φ'_0 values and lesser decrease with increasing reaction time suggest lower coverage.

An overall summary of the relative initial quantum yields is represented in table I. Methanol proved to be less rapidly oxidizable than 1-propanol or propanal.

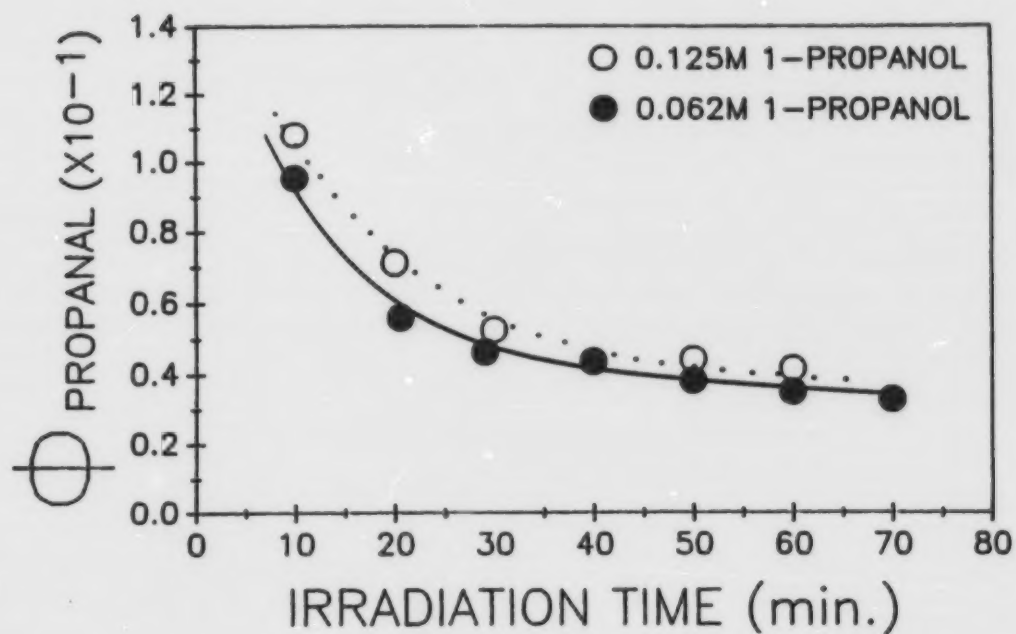


Figure 6 The quantum yields of propanal generated from (o) 0.125M and (●) 0.062M 1-propanol in system I.

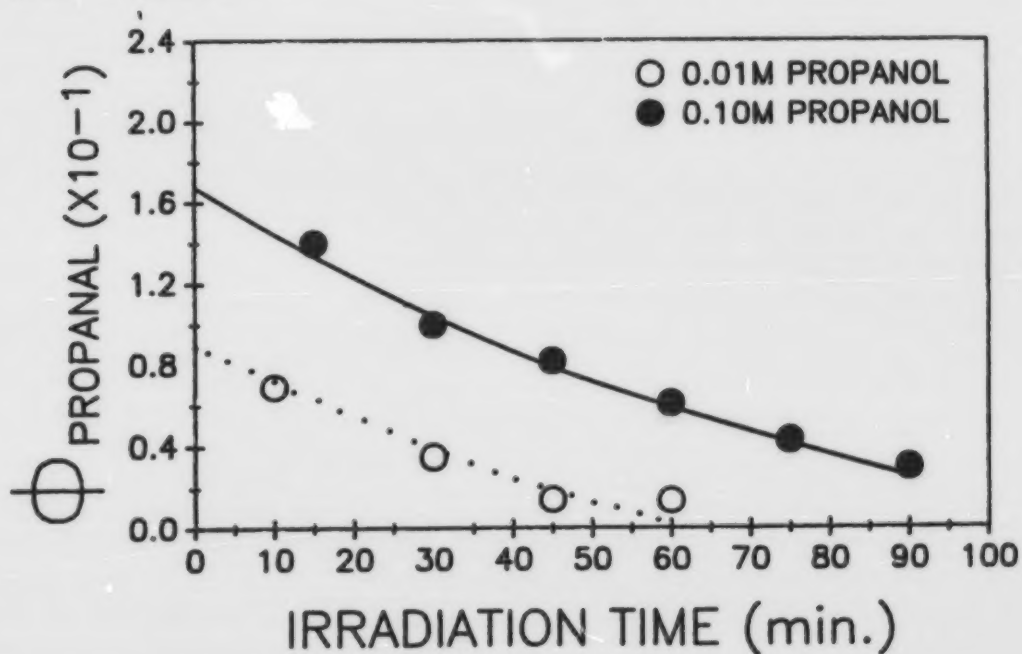


Figure 7 The quantum yields of propanal produced from (o) 0.01M and (●) 0.10M 1-propanol employing system II.

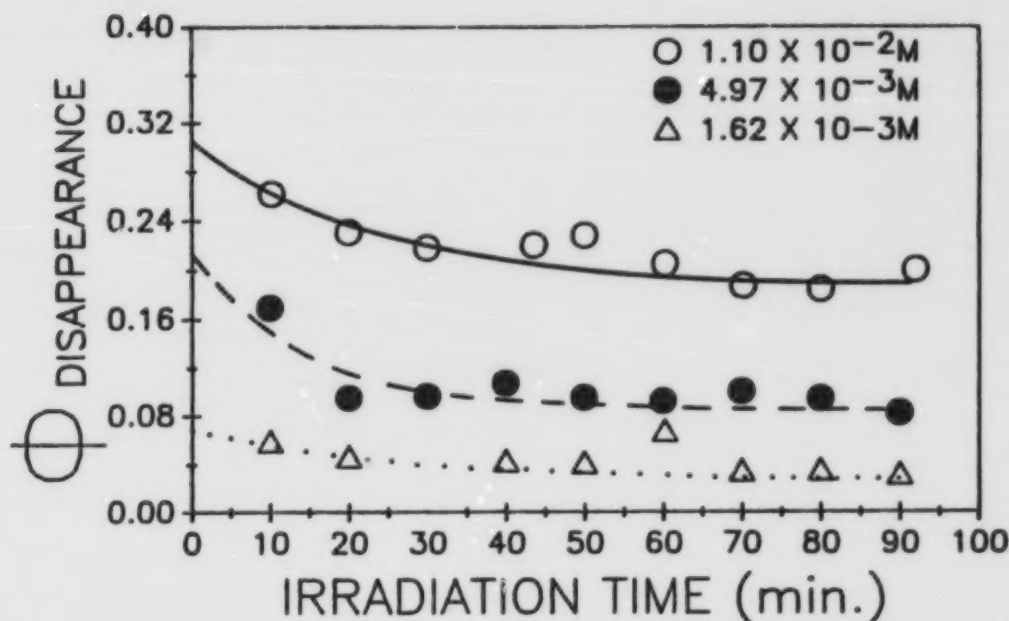


Figure 8 Quantum yields of disappearance of propanal employing system I: $1.10 \times 10^{-2} \text{M}$ (o), $4.97 \times 10^{-3} \text{M}$ (●), and $1.62 \times 10^{-3} \text{M}$ (Δ) propanal.

CONCLUSION:

In this study we report the relative quantum yields of alcohols, employing a commercial photoreactor (stationary TiO_2). The results were compared with TiO_2 dispersions so as to evaluate the efficiency of the photoreactor. TiO_2 easily satisfies the quantum yield criteria $\Phi' > 0.1$, which indicates that search for a superior photocatalytic material is not a priority. The factors limiting consumption of a substrate relate to its reaction rate on the surface of the photocatalyst (which may be linked to its redox potential), mass transport to the surface, desorption and competition for surface sites. The intermediates formed during photoreactions were often more oxidizable and tended to be further decomposed in competition with desorption from the surface.

These results are in agreement with our earlier work, emphasising the direct reaction of the organic molecule, on the surface of the photocatalyst as opposed to catalyst generation of radicals [7].

ACKNOWLEDGMENT:

We would like to thank the Concordia Ecotoxicology Laboratories, Dr. P. Anderson for providing access to the instruments, Mr. P. Aysola for technical assistance and Mr. D. Palacios for experimental assistance. This study has been supported by grants from NSERC, FCAR du Québec and the MESS du Québec.

TABLE I
Relative Initial Quantum Yields

<u>System</u>	<u>Substrate</u>	<u>Molar</u>	$\Phi'_{\text{dis.}}$	<u>Product</u>	Φ'_0
I	propanol	1.25×10^{-1}	1.7	propanal	0.17
I	propanol	6.20×10^{-2}	1.3	propanal	0.15
I	propanol	1.03×10^{-2}	0.22	propanal	0.019
I	propanal	1.10×10^{-2}	0.27		
I	propanal	4.97×10^{-3}	0.23		
I	propanal	1.62×10^{-3}	0.061		
I	propanal	8.06×10^{-3}	0.028		
II	propanol	1.00×10^{-1}	0.87	propanal	0.17
II	propanol	1.00×10^{-2}	0.72	propanal	0.09
I	methanol	5.63×10^{-2}	0.34		
I	methanol	9.27×10^{-3}	0.082		
I	methanol	4.57×10^{-3}	0.035		

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SESSION 4
CURRENT STATE-OF-THE-ART FIELD
APPLICATIONS AND CASE STUDIES



**UV/OXIDATION OF ORGANIC CONTAMINANTS
IN GROUND, WASTE, AND LEACHATE WATERS**

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ABSTRACT:

Over the past four years, Ultrox International has demonstrated the efficacy of ultraviolet light-enhanced oxidation at industrial, Department of Defense and Superfund sites. Waters containing halogenated solvents such as trichloroethylene, perchloroethylene and other halogenated compounds have been successfully treated with UV/ozone or UV/hydrogen peroxide or UV with ozone and peroxide. Other contaminants such as benzene, toluene, xylene, hydrazines, phenols, chlorophenols, dioxanes, PCBs and pesticides in wastewaters and groundwaters have also been reduced to acceptable discharge standards. Summations of the above projects will be presented, along with some of the technological basis of this process. Data showing comparisons of UV-enhanced oxidation testing with traditional ozonation also will be presented based upon research conducted under government grants.

Design and cost data from pilot plant testing and from operations at full-scale commercial installations will be presented. The applications will cover ultraviolet/oxidation systems treating waste water in the wood treating industry, rocket fuel waste water, and groundwater containing chlorinated solvents at automotive, aerospace and electronics manufacturers.

A discussion of test results and process economics from a demonstration of the ULTROX¹ process in the U.S. EPA Superfund Innovative Technology Evaluation (SITE) Program also will be presented.

INTRODUCTION:

The removal of low levels of organic contaminants from groundwaters and industrial wastewaters presents a challenge to environmental professionals. Well-known and commonly used treatment processes such as granular activated carbon (GAC) and air-stripping transfer pollutants from one medium to another. With increasing public and regulatory concern over the final fate of pollutants, such transference technologies are not optimal.

Conventional chemical oxidation has been used in the treatment of various waters polluted by organic chemicals for a number of years. Potassium permanganate, chlorine and chlorine dioxide have been used for treating organics such as phenol and its homologs in wastewaters.

¹ ULTROX is a registered trademark.

Hydrogen peroxide with a catalyst such as ferrous sulfate (Fenton's Reagent) has been used for oxidizing phenol and other benzene derivatives. Processes utilizing iron catalyzed peroxides and chlorine compounds are attractive in that they utilize relatively low-cost treatment equipment. The disadvantages of these processes are that they can attack only a limited number of refractory organics, and they produce iron sludges or chlorinated organics. Ozone alone has been used to treat phenolic wastes, cyanides and certain pesticides. Ozone treatment is a very clean process but is limited in the number of compounds which can be treated. These oxidation processes have been used and are continuing to be used in a number of situations.

The use of ultraviolet light catalyzed ozone plus hydrogen peroxide (UV/oxidation) as a water treatment technique is rapidly expanding. It offers a means of solving many of the problems created by the toxic water soluble organic chemicals that are found today in groundwater, wastewater, leachate and drinking water supplies without many of the disadvantages of more conventional treatment techniques.

UV/oxidation, when used as a stand-alone treatment process, or in tandem with some of the above mentioned processes, can cost-effectively destroy or render non-toxic the organic chemicals found on the EPA's priority pollutant list.

This paper describes the experience of Ultrox International in developing and applying the ULTROX UV/oxidation process to the full-scale treatment of organic chemicals in wastewaters, drinking waters, leachates and groundwaters. The oxidants used in these applications are ozone and hydrogen peroxide. Ultrox International was issued a process patent in 1988 covering the application of UV light, ozone and hydrogen peroxide to the treatment of a broad range of organic compounds in water.

DESCRIPTION OF THE UV/OXIDATION PROCESS:

The ULTROX process was developed over a 17 year period. Ultraviolet light, when combined with O_3 and/or H_2O_2 produces a highly oxidative environment.

UV light significantly enhances ozone or H_2O_2 reactivity by:

- I. Transformation of O_3 or H_2O_2 to highly reactive (OH) $^\cdot$ radicals
- II. Excitation of the target organic solute to a higher energy level
- III. Initial attack of the target organic by UV light

The effect of UV enhanced oxidation is illustrated in Table 1.

ULTROX UV/OXIDATION EQUIPMENT:

ULTROX UV/oxidation equipment treatment systems: (1) have very few moving parts, (2) operate at low pressure, (3) require a minimum of maintenance, (4) operate full-time or intermittently in either a continuous or batch treatment mode, (5) utilize efficient, low temperature, long life UV lamps, and (6) can employ the use of a micro-processor to control and automate the treatment process.

The ULTROX UV/oxidation system consists of a UV/oxidation reactor and an oxidation source -- either an ozone generator with an air preparation system and/or a hydrogen peroxide feed system. Figures 1, 2, and 3 show an isometric assembly view, a drawing and a photo of a Model F-650 system, which accommodates flow rates up to 60 gpm or batches of 650 gallons.

The reactor is fabricated from stainless steel. The UV lamps are enclosed within quartz tubes for easy replacement and are mounted vertically within the reactor. Depending upon size of the reactor and the type of water to be treated, the reactor can have 4 to 8 stages. Lamps are installed either in all stages or in designated stages, depending upon the type of treatment specified. When ozone is used as the oxidant, it is introduced at the base of the stage. The ozone is dispersed through porous stainless steel diffusers. The number of diffusers needed will depend upon the type of organics being oxidized and the degree of removal required.

Ozone is produced from either compressed air, dried to a -60°F dew point by desiccant columns, or produced from liquid oxygen. Up to 2% wt. ozone is generated from air, and up to 5% wt. ozone can be produced economically from oxygen.

When hydrogen peroxide is used in the process, it is directly metered into the influent line to the reactor.

Within the reactor, the water flows from stage to stage in a sinusoidal path using gravity flow. When the reactor uses ozone, the residual ozone in the off-gas is decomposed back to oxygen by the use of a fixed-bed catalytic unit operating at 150°F. The air is then vented to the atmosphere.

Ozone generators with varying capacities are used with the Model F-650 reactor. The size of generator depends upon the ozone dosage requirements. Present installations use 28 to 150 lb. per day capacities.

APPLICATION OF UV/OXIDATION:

UV/oxidation equipment developed by Ultrox in recent years has been used to treat a wide variety of waste streams. Tables 2 and 3 list toxic compounds found in groundwaters and wastewaters that have been successfully treated with the ULTROX UV/oxidation System. Specific case histories of treatability and design studies for private industries and military installations are presented in Table 4. In each of these cases, pilot treatment plants were operated on site to develop treatment design and economic data.

Contaminants oxidized included: pesticides, aromatics, munitions, and chlorinated solvents.

Table 5 illustrates projects where the treatability and design studies were converted into permanent on-site UV-oxidation installations. The systems to date treat either industrial groundwaters, wastewaters and process waters. Contaminants in these waters include phenols, chlorinated solvents, hydrazine, dimethylnitrosamine, tetrahydrofuran and formaldehyde. Commercial systems have been designed, built and installed to treat flows varying from 10,000 gallons to 300,000 gallons per day. A water supply system to treat 1.3 million gallons per day is under construction.

Standard equipment designs are used in all of these installations. Reactor size varies from 300 gallons to 4,800 gallons. Ozone generators range from 21 lb. to 140 lb per day. In several cases hydrogen peroxide is used in place of or with ozone.

Treatability studies are carried out first in the laboratory using glassware equipment to determine the feasibility of treating the water with UV/O₃, UV/H₂O₂, or UV/O₃/H₂O₂.

If the results are encouraging, the next step in the study involves the installation of a skid-mounted pilot plant on site. Sufficient design and economic data normally are collected within 2 weeks. Specifications for the full-scale system are then prepared. Standard reactors, ozone generators and hydrogen peroxide feed systems are utilized. Systems are assembled and tested at our facilities and then shipped to the job site. The systems are then installed, checked out, and turned over to the customer. Full service maintenance contracts are

available.

Full-scale systems, in most cases, are automated using microprocessor control. The system usually requires periodic monitoring (once per shift or once per day). The systems are designed to operate in a batch or continuous mode depending upon treatment requirements.

In a number of cases, UV-oxidation is used as a part of a treatment train. For example, at wood treating sites prior to the UV-oxidation treatment, the wastewater or groundwater requires breaking of oil/water emulsions and removal of suspended matter, as well as adjustment of pH.

**CASE STUDY: EPA SITE PROGRAM - LORENTZ BARREL AND DRUM SITE
 SAN JOSE, CA**

The EPA has established a formal program to accelerate the development, demonstration, and use of new or innovative technologies to be used in site cleanups. This program, called the Superfund Innovative Technology Evaluation (SITE) program, has four goals:

- . To identify and, where possible, remove impediments to the development and commercial use of alternative technologies.
- . To conduct a demonstration program of the more promising innovative technologies for the purpose of establishing reliable performance and cost information for site characterization and cleanup decision-making.
- . To develop procedures and policies that encourage selection of available alternative treatment remedies at Superfund sites.
- . To structure a development program that nurtures emerging technologies.

Each year, EPA solicits proposals to demonstrate innovative technologies. To identify the best available technologies, an extensive solicitation is necessary. A screening and selection process follows, based on four factors: (1) the technology's capability to treat Superfund wastes, (2) the technology's performance and cost expectations, (3) the technology's readiness and applicability to full-scale demonstrations, and (4) the developer's capability and approach to testing.

In the third year of the SITE program, Ultrox was selected to demonstrate their UV/oxidation technology. The Lorentz Barrel and Drum Superfund site in San Jose, California was selected for the demonstration.

The Lorentz site was used for drum recycling for nearly 40 years. Over this period of time, the site received drums from over 800 private companies, military bases, research laboratories, and county agencies in California and Nevada. Drums arrived at the site containing residual aqueous wastes, organic solvents, acids, metal oxides, and oils.

Since 1968, there have been several regulatory actions at the Lorentz site. In 1987, the Lorentz facility ceased operation and the EPA assumed lead agency responsibility for the site

remediation. Investigations revealed that the groundwater beneath the site was contaminated with a number of chlorinated solvents, chlordane, toxaphene and PCBs.

An ULTROX P-150 pilot plant was moved in on February 21, 1989. Thirteen (13) tests were conducted between February 24 and March 9, 1989, on extracted groundwater from the site. During the treatability bench studies, TCE and TCA were chosen to monitor the progress of the pilot.

Figures 4 and 5 illustrate analysis of the waste stream influent and the treated effluent for the targeted contaminants.

The technical application report has been issued by the EPA, and the application analysis report is being reviewed. Based on the results, the ULTROX UV/oxidation process was successful in the reduction of all of the VOCs present in the groundwater at the Lorentz site to below drinking water standards. The bicarbonate level of the groundwater was extremely high (1200 mg/l). Because of this, treatment costs are higher than what would be experienced in more normal groundwater applications. Based on the conditions tested at the site, treatment costs were estimated to be as follows:

Flow Rate:	100 gpm
Influent Concentration:	250-1000 μ g/l VOCs, pesticides, PCBs
Effluent Concentration:	<10 μ g/l
Treatment Costs:	<u>\$/1000 gallons</u>
Ozone (@ 0.06/KWH)	\$ 0.370
H ₂ O ₂ (@ \$0.75/lb)	0.156
UV (incl. power and annual lamp replacement)	<u>0.836</u>
O & M Cost	1.36
Capital Amortization (16%/year)	<u>0.75</u>
Total Treatment Cost:	\$ 2.11/1000 gallons

CASE STUDY: AUTOMOTIVE PARTS MANUFACTURER, MICHIGAN

Testing of water beneath a Michigan automotive parts manufacturer revealed significant VOC contamination. TCE levels of 5,000 to 10,000 μ g/l were recorded as well as trace levels of

other chlorinated solvents. The Michigan Department of Natural Resources required that the manufacturer pump and treat the groundwater.

The manufacturer investigated air stripping with GAC off-gas treatment, aqueous phase GAC and ULTROX UV/oxidation as possible treatment alternatives. Bench scale studies were conducted at a GAC supplier and at Ultrox's laboratory. While all treatment techniques could provide the required removal levels, UV/oxidation was the most economical. An ULTROX P-75 pilot scale treatment system was delivered to the site. Testing over a two week period confirmed the data obtained in the laboratory. An ULTROX F-3900 treatment system was ordered and installed in May, 1989. The system is currently operating and achieving the following results, which exceed Michigan requirements:

Flow Rate:	210 gpm
Influent Concentration:	5500 $\mu\text{g/l}$ TCE
Effluent Concentration:	1 $\mu\text{g/l}$ TCE
Treatment Costs:	<u>\$/1000 gallons</u>
Ozone (@ 0.06/KWH)	\$ 0.119
H ₂ O ₂ (@ \$0.75/lb)	0.188
UV (incl. power and annual lamp replacement)	<u>0.133</u>
O & M Cost	0.44
Capital Amortization (16%/year)	<u>0.29</u>
Total Treatment Cost:	\$ 0.73/1000 gallons

UV/OXIDATION TREATMENT AND OPERATING COSTS:

Table 6 presents the actual costs of treating by UV/oxidation wastewater and groundwaters at various permanent industrial installations. Some of these costs are in the cents per thousand gallon range and others in cents per gallon range.

In the case of the hydrazines, a small volume of water is treated per day on a batch basis and a comparatively long reaction time is needed. UV/oxidation was found to be the most cost-effective method of destroying the three types of hydrazines and the nitrosamine which is formed as a by-product by the oxidation. The UV/oxidation system replaced a chlorination unit, which produced chlorinated organic by-products.

The price range of UV/oxidation equipment at various installations cited in Table 7 varies from \$45,000 to \$440,000 (uninstalled). Pricing depends upon the oxidant requirement - whether ozone or hydrogen peroxide is used, the chemical structure of the organic compounds treated, the number of UV lamps required, and the retention time required to achieve an acceptable discharge standard.

SUMMARY:

Over the last 17 years, UV/oxidation has progressed from research and development to commercial operation. During these years, Ultrox has advanced its design through applied bench testing, pilot studies, and full-scale systems that remove contaminants from a wide variety of wastewaters and groundwaters.

UV/oxidation technology is not suitable for every organic contamination problem. It can, however, effectively address a wide range of clean-up needs. This form of on-site chemical oxidation can offer real advantages over conventional treatment techniques and should be considered when evaluating water treatment alternatives.

TABLE 1

OXIDATION OF METHYLENE CHLORIDE

<u>TIME</u> <u>(MIN.)</u>	<u>CONTROL</u>	<u>UV</u>	<u>UV/H₂O₂</u>	<u>O₃/H₂O₂</u>	<u>UV/O₃</u>	<u>UV/O₃/H₂O₂</u>
0	100	100	100	100	100	100
15	100	59	46	32	36	19
25	100	42	17	21	16	7.6

OXIDATION OF METHANOL

<u>TIME</u> <u>(MIN.)</u>	<u>CONTROL</u>	<u>UV</u>	<u>UV/H₂O₂</u>	<u>UV/O₃</u>	<u>UV/O₃/H₂O₂</u>
0	75	75	75	75	75
30	75	75	75	31	1.2

CONCENTRATIONS = mg/l

TABLE 2

Industrial effluents containing:

Amines	Methylene Chloride
Aniline	PCB's
Benzene	Pentachlorophenols
Chlorinated Solvents	Pesticides
Chlorobenzene	Phenol
Complex Cyanides	RDX
Creosote	TNT
Hydrazine Compounds	Toluene
Isopropanol	Xylene
MEK	Polynitrophenols
MIBK	

TABLE 3

Groundwaters containing:

BTX	PCE
Creosote	Pentachlorophenol
1,2 DCA	bis (2-chloroethyl) ether
DCEE	Pesticides
Dioxins	Polynuclear Aromatics
Dioxanes	1,1,1 TCA
Freon 113	TCE
MeCl ₂	THF
MIBK	Vinyl Chloride
PCBs	Triglycol dichloride ether

TABLE 4

TREATABILITY AND DESIGN STUDY RESULTS USING PILOT PLANTS ON SITE

<u>Customer</u>	<u>Application</u>	<u>Contaminants</u>	<u>Results</u>
Bulk Chemical Transfer Depot	Contaminated groundwater	TCE, PCE, methylene chloride	Water treated and reinjected into ground
Municipal Water Producers	Contaminated drinking water supply	TCE, PCE, color	VOCs and color reduced to below state action levels
Aerospace Co.	Paint stripping wastewater	Methylene chloride	MeCl ₂ reduced from 4000 ppm to less than 100 ppb
Chemical Co.	Wastewater	Misc. pesticides (including DBCP)	DBCP and other pesticides reduced to less than 1 ppb
Automotive Co.	Groundwater	TCE, MeCl ₂	Reduced 10 ppm to 5.0 ppb
Electronics Co.	Wastewater/runoff water, groundwater	PCBs, ViCl, DCA + other VOCs	Reduced PCBs to less than 1 ppb; VOCs reduced to below state action levels
Munition Plants	Wastewater	TNT, RDX	TNT & RDX reduced from 100 ppm to less than 1 ppm
Army Bases	Contaminated groundwater	DIMP, DBCD, VOCs	DIMP & DBCD reduced to less than 10 ppb; VOCs reduced to below state action levels
Semiconductor Co.	Wastewater	EDTA	Reduced EDTA from 6,000 ppm to 100 ppm (acceptable discharge standard)
Petrochemical Mfr.	Wastewater	Benzene	Reduced benzene from 10 ppm to 50 ppb
Semiconductor Mfr.	Groundwater	benzene, toluene, xylene, ethyl benzene	Reduced contaminants from 14.0 ppm to 4.0 ppb

TABLE 5

FULL-SCALE ULTROX SYSTEMS

<u>Customer</u>	<u>Application</u>	<u>Contaminants</u>	<u>Results</u>
Wood Treating Plants (2)	Wood treating wastewater	Phenol, pentachlorophenol	Water treated and discharged to POTW
Closed Wood Treating Plant	Contaminated groundwater	Phenol, pentachlorophenol	Water treated and discharged to POTW
Chemical Plant	Fume scrubbing water	Hydrazine, monomethyl hydrazine, unsymmetrical dimethyl hydrazine	Destroyed parent compounds to N.D. levels and dimethyl nitrosamine below 10 ppb
Automotive Foundry	Contaminated groundwater	TCE, Trans 1,2-DCE	Water treated and discharged to lake
Aerospace Co.	Contaminated groundwater	TCE, TCA, DCA, PCE MeCl ₂ , vinyl chloride	Water treated and discharged to POTW
Chemical Plant	Wastewater	Phenol, formaldehyde	Water treated and discharged to POTW
Semiconductor Co.	Contaminated groundwater	THF	Replaced a GAC system to reduce THF from 1,000 ppb to less than 5 ppb
City of Drinking Water	Contaminated	PCE to be injected into water supply	After testing treated water South Gate, CA
U.S. Mint	Wastewater	Cyanides	Water to be treated and discharged to POTW
Photocopy Company	Groundwater	TCE, Toluene, PCE TCA, Vinyl Chloride 1,1 DCA	Water to be treated and polished prior to discharging to storm sewer

TABLE 6

DIRECT OPERATING & MAINTENANCE COSTS FOR UV-OXIDATION
AT INDUSTRIAL AND MUNICIPAL INSTALLATIONS

<u>Type of Water</u>	<u>Contaminants</u>	<u>Contaminant Concentration</u>	<u>Discharge to</u>	<u>Volume Treated Per Day</u>	<u>Direct O & M Cost Range</u>
Wood Treating Wastewater	Pentachloro- phenol and phenol	150 ppm	POTW	30,000 gal.	\$1.25-1.35/1000 gal
Wood Treating Groundwater	Pentachloro- phenol and phenol	5 ppm	POTW	86,400 gal.	\$0.90-\$1.00/1000 gal
Contaminated Groundwater	TCE, trans DCE MeCl ₂	5 ppm	Surface Water	300,000 gal.	\$0.47/1000 gal
Contaminated Groundwater	TCE, TCA, DCA, PCE, MeCl ₂ , ViCl	600 ppb	POTW	72,000 gal.	\$0.33/1000 gal
Contaminated Groundwater	THF	1 ppm	Ground	216,000 gal.	\$0.39/1000 gal
Contaminated Drinking Water Supply	PCE	5-10 ppb	Water Supply	1.4 m. gal.	\$0.05-0.10/1000 gal.
Wastewater	Cyanides	2-5 ppm	POTW	72,000 gal.	\$1.50-1.90/1000 gal.
Groundwater	TCE, PCE Toluene TCA	7-10 ppm	Storm Sewer	360,000 gal.	\$1.25-\$1.40/1000 gal.

TABLE 7

TYPICAL CAPITAL COSTS FOR UV-OXIDATION SYSTEMS

Type of Water	Contaminants	Total Contaminant Concentration	Water Flow Rate (GPD)	Price Range (uninstalled) \$
Wood Treating Wastewater	Pentachloro- phenol Phenol	150 ppm	30,000	125,000-150,000
Wood Treating Groundwater	Pentachloro- phenol Phenol	5 ppm	86,400	175,000-200,000
Fume Scrubber Water	Hydrazines	5,000 ppm	600-1500	125,000-150,000
Contaminated Groundwater	TCE, trans DCE MeCl ₂	5 ppm	300,000	225,000-275,000
Contaminated Groundwater	TCE, TCA, DCA PCE, MeCl ₂ , ViCl	600 ppb	72,000	130,000-150,000
Contaminated Groundwater	THF	1 ppm	216,000	250,000-300,000
Wastewater	Phenol	90 ppm	4,300	45,000-55,000
Contaminated Drinking Water	PCE	5-10 ppb	1.4 million	275,000-325,000
Waste Water	Cyanides	2-5 ppm	72,000	400,000-440,000
Ground Water	TCE, PCE, Toluene, TCA	7-10 ppm	360,000	300,000-350,000

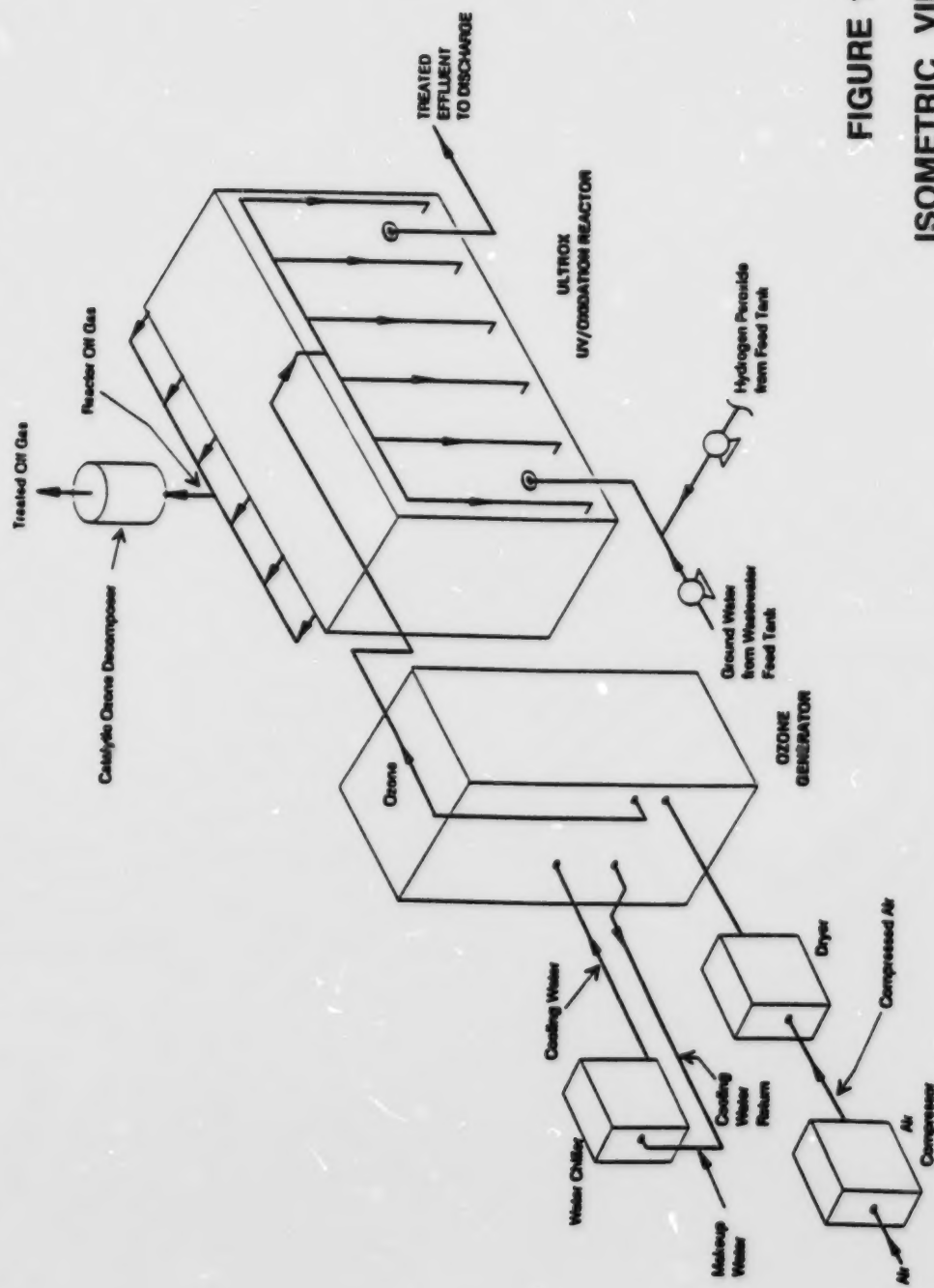


FIGURE 1
ISOMETRIC VIEW OF
ULTROX SYSTEM

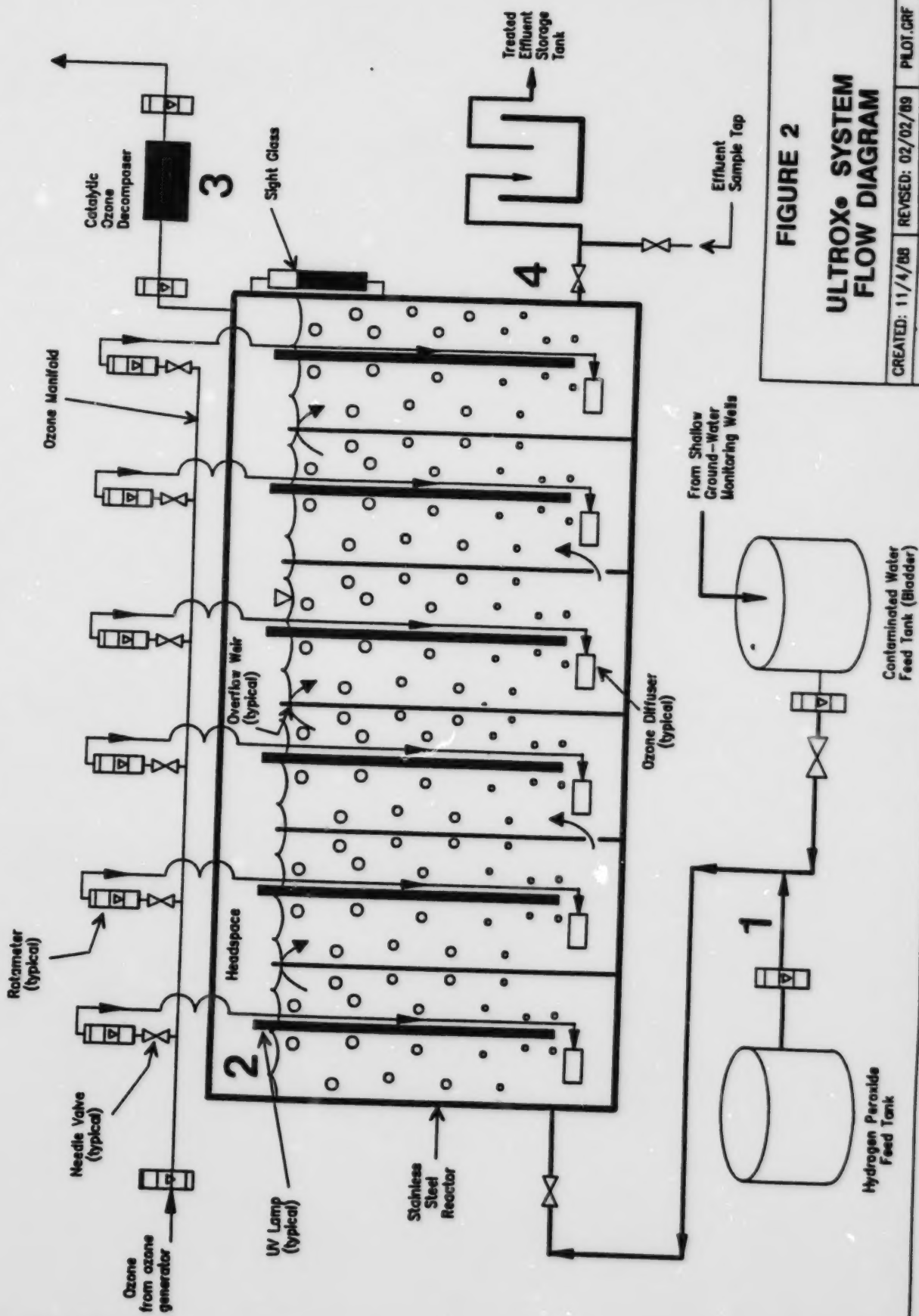


FIGURE 2

ULTROX® SYSTEM FLOW DIAGRAM

MODEL F-650 SYSTEM

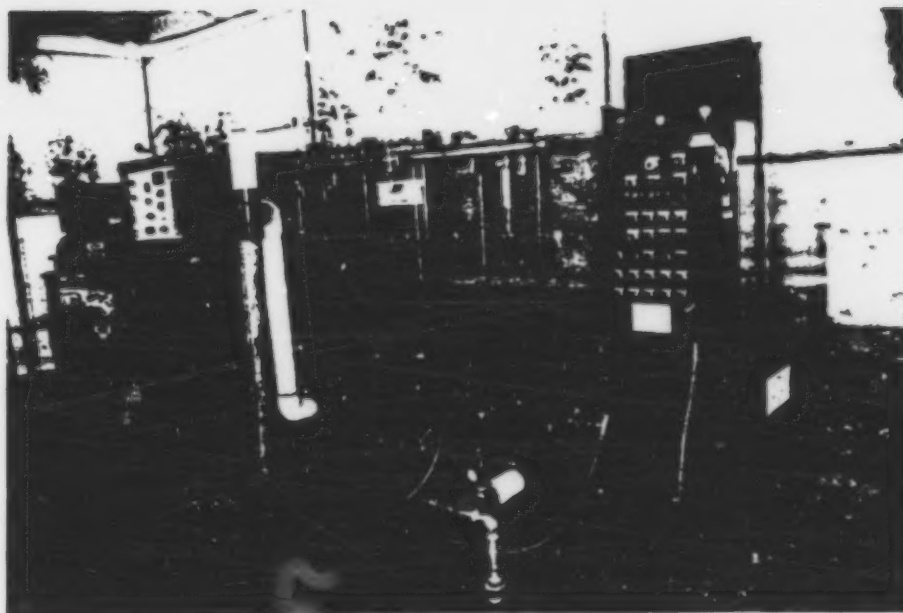


FIGURE 3

ULTROX SITE DEMONSTRATION TCE REMOVAL

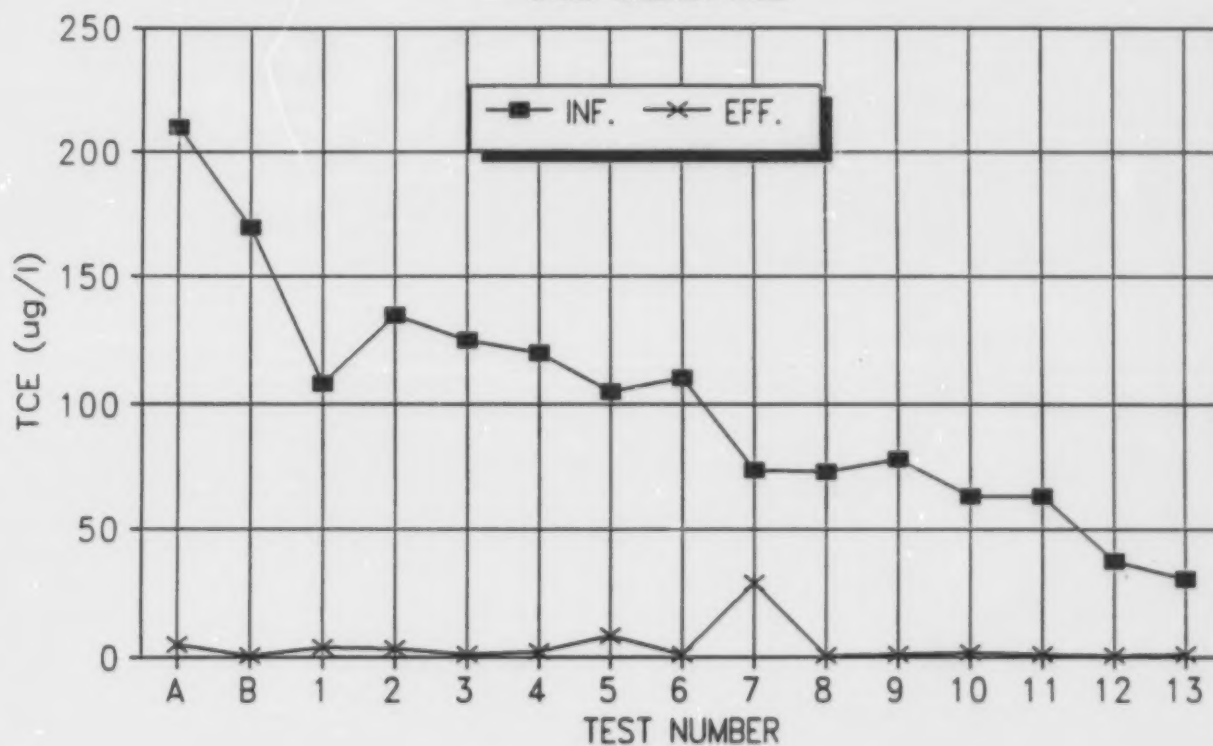


Figure 4

ULTROX SITE DEMONSTRATION TCA REMOVAL

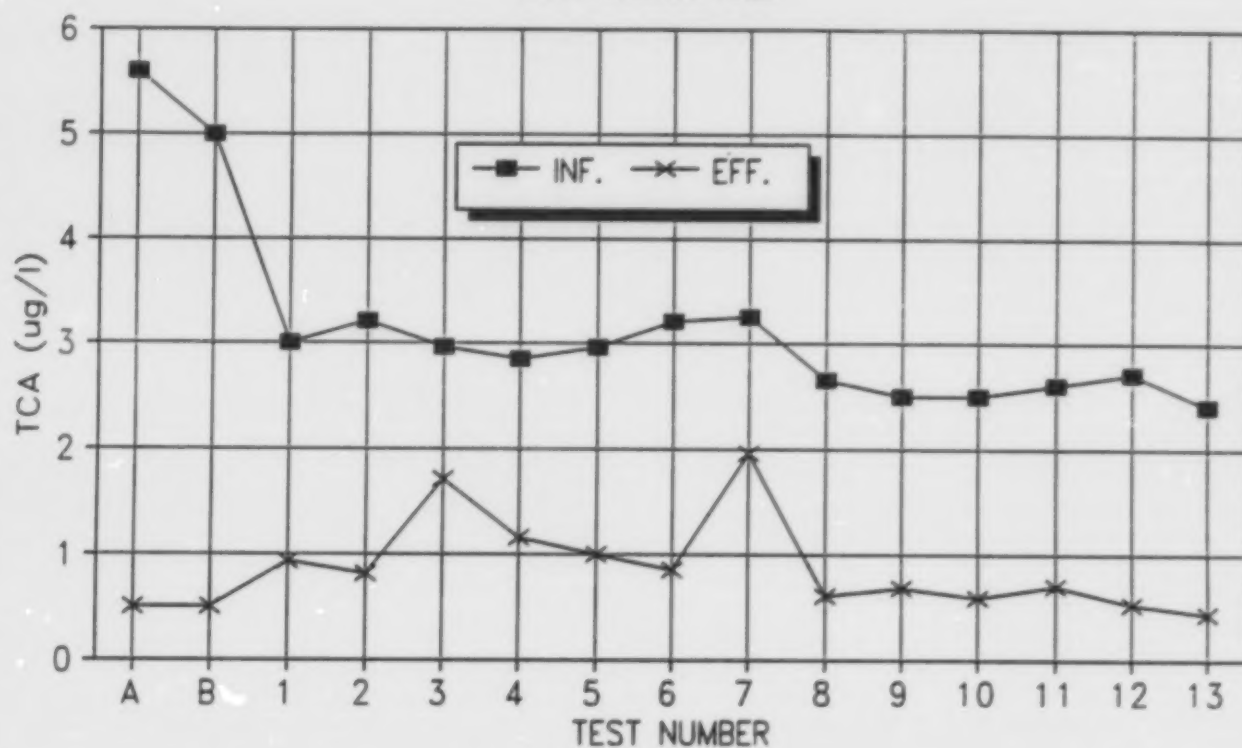


Figure 5

**RAYOX: A SECOND GENERATION ENHANCED OXIDATION
PROCESS FOR GROUNDWATER REMEDIATION**

**Stephen R. Cater, Keith G. Bircher
and R.D. Samuel Stevens
SOLARCHEM ENVIRONMENTAL SYSTEMS**

ABSTRACT

The Rayox water decontamination system represents a second generation enhanced (advanced) oxidation water remediation technology. Several key features of the Rayox system give it substantial performance advantages over previous embodiments of enhanced oxidation technology. These features are discussed along with their impact upon system performance. Results from several case studies on groundwater treatment demonstrate Rayox's powerful and versatile capability.

INTRODUCTION

The use of enhanced oxidation processes to clean up contaminated groundwater and industrial process wastewater streams has become increasingly more common in the past few years. It is becoming more widely realized that enhanced oxidation offers considerable advantages over more traditional treatment approaches such as air stripping, activated carbon or reverse osmosis. These techniques do not destroy the pollutants but merely transfer them from water into another medium. Enhanced oxidation results in the destruction of waterborne contaminants in a convenient cost-effective manner, with no secondary disposal requirements.

This paper gives a brief review of the enhanced oxidation process followed by a description of the Rayox second generation enhanced oxidation system and its advantages. Results of several case studies are presented showing the application of Rayox in the treatment of contaminated groundwater. Although outside the scope of this paper, the Rayox system has also been successfully applied to industrial process wastewater streams, and these results can be found elsewhere.^{1,2}

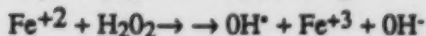
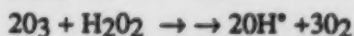
THE ENHANCED OXIDATION PROCESS

Traditional oxidation processes for the remediation of contaminated water have utilized oxidants such as molecular ozone, hydrogen peroxide or hypochlorite. The application of these substances for the remediation of contaminated water, to the increasingly more stringent requirements posed by current and pending regulations, is restricted by their selectivity and the long contact times typically necessary to achieve the required degree of contaminant destruction. In enhanced oxidation, the rates of oxidation are greatly enhanced over those using conventional oxidants, because of the participation of radical species, principally the hydroxyl radical ($\text{HO}^\bullet$). The hydroxyl radical is a very powerful oxidizing agent which reacts very rapidly with virtually all organic compounds. The rate of attack by hydroxyl radical is typically one million (10^6) to one billion (10^9) times faster than the corresponding attack with molecular ozone, as shown in Table 1.

Table 1
REACTION RATES OF OZONE AND HYDROXYL
RADICALS WITH CLASSES OF ORGANIC COMPOUNDS

COMPOUND	k, in $\text{L mole}^{-1} \text{s}^{-1}$	
	O_3	OH
Olefins	1 to 450×10^3	10^9 to 10^{11}
S-containing organics	10 to 1.6×10^3	10^9 to 10^{10}
Phenols	10^3	10^9
N-containing organics	10 to 10^2	10^8 to 10^{10}
Aromatics	1 to 10^2	10^8 to 10^{10}
Acetylenes	50	10^8 to 10^9
Aldehydes	10	10^9
Ketones	1	10^9 to 10^{10}
Alcohols	10^{-2} to 1	10^8 to 10^9
Alkanes	10^{-2}	10^6 to 10^9
Carboxylic acids	10^{-3} to 10^{-2}	10^7 to 10^9

There are several methods of generating hydroxyl radicals from ozone and/or hydrogen peroxide and ultraviolet (UV) light, which have been described by several authors.⁴⁻⁷ Three common methods are: the photolysis of hydrogen peroxide with ultraviolet light, the reaction between ozone and hydrogen peroxide and the use of Fenton's reagent. These approaches can be described by the following simplified chemical equations:



Once the hydroxyl radical is generated, it attacks the contaminants in solution and initiates a rapid, oxidative cascade of reactions. The ultimate products of this oxidative cascade are CO_2 and H_2O (and Cl^- in the case of chlorinated organic compounds). As with virtually all oxidation processes in solution, the complete, step by step, reaction mechanism is complex and has not been elucidated for many compounds, and then only under a rather narrow set of conditions. For example, the mechanism of the $\text{HO}^\bullet$ radical initiated oxidation of CHCl_3 , shown in Figure 1, has recently been proposed by Getoff.⁸ In this proposed mechanism, the initial step is an abstraction of a hydrogen atom by the $\text{HO}^\bullet$ radical to yield water and the trichloromethyl radical ($^\bullet\text{CCl}_3$). Once formed, the $^\bullet\text{CCl}_3$ radical continues down the oxidative cascade by one of two routes: reaction with dissolved oxygen to yield the trichloroperoxy methyl radical ($\text{CCl}_3\text{O}_2^\bullet$) or, it reacts with any hydrogen peroxide present, to yield HCl , $\text{HO}^\bullet$ and COCl_2 . Once formed, the COCl_2 would be rapidly transformed via hydrolysis to HCl and CO_2 . As shown, the $\text{CCl}_3\text{O}_2^\bullet$ radical can oxidize an anion present (e.g. HCO_3^-) to yield the trichloroperoxymethyl anion (CCl_3O_2^-) which reacts with water to yield COCl_2 , HCl and the perhydroxyl anion (HO_2^-). As mentioned above, the COCl_2 would be rapidly hydrolysed to HCl and CO_2 while the HO_2^- would be oxidized by any oxidant in solution (e.g. $\text{H}_2\text{O}_2, \text{HO}^\bullet$) to the perhydroxyl radical ($\text{HO}_2^\bullet$).

It should be mentioned that although there is a high degree of confidence that the initial step (hydrogen abstraction by the $\text{HO}^\bullet$ radical) and final products (HCl, CO_2) are as shown, the proposed intermediate reaction scheme is hypothesized in light of the findings of other investigations and has not been conclusively demonstrated; thus, it is less certain which (if either) is the principal reaction pathway to CO_2 and HCl . It is worth noting, however, that in the $\text{OH}^\bullet$ radical initiated oxidation of CHCl_3 , the first step is almost certainly the slowest and thus the rate determining, as the lifetimes of any proposed radical intermediates under

usually encountered conditions would be very short, typically of the order of microseconds.

Therefore, although there exists uncertainty about the finer details of the chemistry of enhanced oxidation processes in aqueous solution, the following general observations can be made:

- the oxidations are radical (e.g. $\text{HO}^\bullet$) initiated and are typically much faster than those obtained with traditional oxidants such as H_2O_2 or hypochlorite
- there is a complex, multistep process involving the participation of several, short lived radical intermediates
- the ultimate products are CO_2 , H_2O and HCl (H^+ and Cl^-) when the contaminant is a chlorinated organic compound

THE RAYOX SYSTEM

The Rayox System is essentially comprised of one or more vertical cylindrical reactors containing a Solarchem proprietary high power UV lamp, a quartz sleeve, a transmittance controller to prevent the sleeve from fouling and a stainless steel outer wall. A Rayox system also has provision for the injection of substances such as H_2O_2 , O_3 , or proprietary rate enhancing ENOX additives. A sample flow schematic is shown in Figure 2. This design allows for great flexibility in the selection of the optimum process configuration in terms of lamp selection, source of radicals (e.g. H_2O_2 or O_3), reactor diameter, staged treatment, etc.

The Solarchem lamps are proprietary high intensity UV light sources which have enhanced output where pollutants are photochemically most active. This results in the creation of an important additional destruction pathway besides hydroxyl radical attack. This becomes especially important in the treatment of refractory compounds such as carbon tetrachloride, chloroform or trichloroethane, which react relatively slowly with hydroxyl radical. While many organic compounds have rate constants for reaction with hydroxyl radical of between 10^8 - $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, compounds such as carbon tetrachloride, chloroform and trichloroethane have rate constants between 10^6 - $10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. This results in a much

longer and more difficult treatment when hydroxyl radical initiated oxidation is the only contaminant destruction mechanism.

The relative importance of photolysis can be determined by comparing the rates of photolysis with the rates of hydroxyl radical attack. The rate of photolysis is proportional to the rate of light absorption (I_{ab}) by the compound and the quantum yield of photolysis, where the quantum yield (ϕ) refers to the number of molecules photolyzed per photon of light absorbed. Mathematically this is expressed as:

$$\text{rate} = \int I_{ab}(\lambda) \phi(\lambda) d\lambda$$

where the integral is over the wavelength region where the pollutant absorbs light. The rate of light absorption (I_{ab}) and the quantum yield are wavelength dependent. It is generally found that both the rate of absorption and the quantum yield of photo dissociation are greater for photons with a wavelength shorter than 300 nm. This is especially true for those whose wavelength is below 250 nm. It is therefore important to have a broad band light source which emits strongly across the spectral region below 300nm, which is a characteristic of the Solarchem lamps. For example, powers in excess of 6000W per lamp below 300 nm are attainable with Solarchem lamps. This not only results in highly compact systems, but means that Rayox can destroy the most refractory of waterborne organic contaminants, as the photo-active absorption bands of virtually all organic or organic-metallic contaminants are accessible by the Solarchem lamps.

Chlorinated alkanes are good candidates for photochemical destruction as the quantum yield of photodissociation into radical fragments is significant for these substances. This begins the oxidative degradation of the contaminants into CO_2 , H_2O and HCl . A postulated mechanism of photo-oxidation of chloroform has recently been postulated by Getoff⁸ and is presented in Figure 3. Photolysis of chloroform results in the elimination of a chlorine atom to give the dichloromethyl ($\text{CHCl}_2^\bullet$) radical. The resulting steps after this stage are not as well established but a reasonable mechanism for degradation to CO_2 , H_2O and HCl has been proposed in the article by Getoff.⁸ The $\text{CHCl}_2^\bullet$ radical can be trapped by oxygen to give the peroxy dichloromethyl radical ($\text{Cl}_2\text{CHOO}_2^\bullet$) which can react in a series of steps similar to the Cl_3CO_2 radical described in Figure 1. The $\text{CHCl}_2^\bullet$ radical is also proposed to react with water to yield HCl and formic acid, the latter being oxidized by hydroxyl radical and oxygen into CO_2 and H_2O . As can be seen, the types of reaction in the oxidative cascade are very similar for both the $\text{HO}^\bullet$ and photo dissociation initiated processes.

Another potential benefit of having a sufficient intensity of light of suitable photon energy is the photolysis of any intermediate species that might be produced in the oxidation cascade, thereby accelerating the clean up process. For example, the perhydroxyl radical ($\text{HO}_2^\bullet$) is known to absorb light strongly ($\epsilon \sim 1300 \text{ L mol}^{-1} \text{ cm}^{-1}$) at 230 nm and photodissociates with a high quantum yield ^{9,10} into $\text{HO}^\bullet$ radicals and O atoms according to the following equation:



This process results in the conversion of $\text{HO}_2^\bullet$ into $\text{HO}^\bullet$ radicals, a more powerful oxidant, which can aid in the oxidation process.

Therefore, by utilizing a high power, broad based light source, such as the Solarchem lamps, the water remediation process can be significantly accelerated as a result of the photolysis of the initial contaminants or of any intermediate or by-product that might be produced.

By selection of the optimum reactor design and use of one of the Solarchem lamps, rate enhancements of 3 times are possible for the oxidation of refractory compounds compared to oxidation induced by the hydroxyl radical alone. This can result in a much more cost-effective treatment for these types of compounds.

Another unique design feature in the Rayox system is a transmittance controller, which wipes the quartz sleeve free of any residue. In most applications, fouling can occur due to the presence of iron, suspended solids, high alkalinity, etc. These can rather rapidly accumulate on the quartz sleeve and seriously reduce the amount of light transmitted to the water, resulting in greatly reduced performance. The Rayox system is designed so that the quartz sleeve always remains clean for continued optimum performance.

The Rayox system is highly modular. Each reactor is a separate entity and the type of treatment can be altered in each reactor. In this way, greater flexibility is obtained in achieving the optimum system design treatment. The reactors can be different sizes and one, for example, may involve UV/ H_2O_2 treatment and another may be UV only, depending upon the characteristics of each contaminated water stream.

The final performance enhancing feature of the Rayox System to be discussed in this paper are the ENOX additives. These additives can enhance either the rate of hydroxyl radical generation or the efficiency of their utilization. They are proprietary chemicals which are injected where they would result in the most cost-effective treatment. These additives are consumed during the Rayox treatment and leave no toxic or harmful residual. One example demonstrating the use of an ENOX additive is with the treatment of pentachlorophenol. Pentachlorophenol wastes are widespread in the wood treating industry. We have found that addition of sodium carbonate in the Rayox treatment can increase the rate of removal of pentachlorophenol in some wood treating effluents. This ENOX application has recently been patented (U.S. patent application No. 234, 044; Notice of Allowability March 21, 1990). When carbonate is added to the system it reacts with hydroxyl radical to generate the carbonate radical anion ($\text{CO}_3^{\cdot-}$) and hydroxide ion. The carbonate radical anion is more selective than the hydroxyl radical and attacks pentachlorophenol with greater specificity. This results in less hydroxyl radical "wastage", allowing for a more cost-effective oxidation of the pentachlorophenol.

CASE STUDIES

Solarchem has recently carried out several laboratory and on-site treatments of contaminated groundwater in both Canada and the U.S.A. Some representative results are presented in the following examples. The x-axis on the graphs is given in terms of Rayox dose. This is a composite operating cost term and includes costs for : electrical power, lamp replacement, oxidant (e.g. H_2O_2) and ENOX additives. The Rayox dose in each case study has not been normalized and therefore, a dose of 1 unit in one example is not the same cost as a dose of 1 unit in a different example.

The Solarchem pilot scale testing procedure generally involves the use of large volumes of sample water: 80-210 L is the range of volumes used in batch testing and flowthrough test flow rates range from 20 Lpm to 200 Lpm. On-site demonstrations employ similar flow rates. This approach results in the use of conditions closer to those employed in full scale systems and thus allows for simpler and more reliable scale-up calculations. Figure 4 shows one of Solarchem's transportable, pilot scale RAYOX systems, of the type used in the following case studies. It is noteworthy that as ozone was not used in any of the following applications, there was not a requirement to treat off gases containing stripped VOCs or residual O_3 .

PAHs and Phenols

The groundwater beneath a wood treating plant in Alabama is contaminated with various polycyclic aromatic hydrocarbons, along with phenol, cresol and pentachlorophenol. Tests using Rayox showed that all the compounds could be reduced to below the detection limit from initial concentrations of around 1-2ppm total PAHs and 2ppm total phenols, as indicated in Table 2. Detection limits were around 1 ppb for all compounds and analysis of the treated water was by GC/MS.

Table 2

Rayox destruction of PAHs and Phenols

Compound	Initial Concentration, ppb	Total concentration,ppb
naphthalene	817	ND (<1)
2-methylnaphthalene	223	ND (<1)
1-methylnaphthalene	153	ND (<1)
acenaphthene	187	ND (<1)
fluorene	92	ND (<1)
phenanthrene	433	ND (<1)
phenol	807	ND (<1)
o-cresol	539	ND (<1)
m/p-cresol	698	ND (<1)
2,4-dimethylphenol	698	ND (<1)
pentachlorophenol	56	ND (<2)

A Rayox system to treat 105 gpm of this water is currently being installed at the site. The flow schematic of this system was presented in Figure 2. This system, built to treat more than 100 gpm, occupies a floor space of approximately 8'x 10', illustrating the compact size of a typical Rayox system.

N-Nitrosodimethylamine

The drinking water wells of a community in Elmira, Ontario (100 km northwest of Toronto) are contaminated with n-nitrosodimethylamine (NDMA). Pilot scale Rayox testing showed that the NDMA concentrations were readily reduced to below detection limits (3 ppt) from up to 20 ppb of initial concentrations, as show in Figure 5.

The results demonstrated the high performance of the Solarchem lamp as no addition of peroxide was required to destroy the NDMA. The full scale system to treat 600 US gpm is to be delivered in June, 1990.

VOC's

A contaminated aquifer in New Jersey contains chlorinated solvents of which vinyl chloride, (VC) dichloroethylene (DCE) and trichloroethylene (TCE) are the major components. This groundwater has a very high hardness and contains high concentrations of iron which makes air stripping less desirable because of scaling problems.

The results, presented in Table 3 of an on-site trial using a Rayox mobile unit showed that the VC, DCE and TCE concentrations were consistently reduced to below detection limits - greater than 99.999% destruction.

Table 3
Rayox Treatment of VOCs

<u>Compound</u>	<u>Initial ppb</u>	<u>Treated ppb</u>
VC	1250	< . 1
DCE	18600	< . 1
TCE	14000	< . 1

Gasoline

A groundwater in New Brunswick was contaminated with the gasoline constituents benzene, ethyl benzene, toluene, and xylene (BETX). An on-site trial using a transportable **Rayox** system showed that the concentration of all of the BETX compounds and total petroleum hydrocarbons (TPH) were reduced to drinking water standards. Figure 6 graphically presents some representative results.

Refractory Compounds

Two recent on-site tests demonstrated the ability of **Rayox** to destroy refractory compounds. In the first example, a groundwater aquifer in California is contaminated with up to 25 ppm of dichloroethane (DCA) along with PCP and BETX. Results of the on-site **Rayox** testing showed that all compounds were successfully treated and the DCA could be destroyed to discharge levels of <25ppb (>99.9% of destruction) at a cost which was competitive with activated carbon.

The second example presents results on a variety of refractory compounds. A groundwater aquifer beneath a semiconductor manufacturer in California is contaminated with a variety of chlorinated solvents including dichloroethane (DCA), dichloroethylene (DCE), trichloroethane (TCA), trichloroethylene (TCE) and Freon-113. **Rayox** testing results, presented in Table 4, showed that all compounds including the refractory DCA, TCA and Freon were destroyed to below discharge requirements. The analytical detection limit claimed by the analytical laboratory was about 0.5 ppb for all compounds.

Table 4

Treatment of Refractory Compounds

Compounds	Inlet,ppb	Treated,ppb
DCA	2.3	1.0
DCE	520	0.8
TCA	5.4	1.0
TCE	260	0.6
Freon	81	2.5

Particularly noteworthy is the destruction of the Freon, which is largely the result of photolysis, as the $\text{HO}^\bullet$ reaction rate constant for Freon is $\sim 6 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$.

1,4 Dioxane

The groundwater beneath a chemical manufacturing plant has been contaminated with high concentrations of 1,4 - dioxane. On-site trials using a **Rayox** system showed that the customer could easily attain the proposed discharge requirements of 0.3 ppm. Figure 7 presents some of the typical results.

PCBs

A decommissioned waste storage facility in Ontario has groundwater that is contaminated with trichloroethylene (TCE), trichlorobenzene and PCBs. **Rayox** results showed that all compounds were destroyed to below detection limits. Figure 8 presents some representative destruction curves for TCE and PCB. As was found in the destruction of Freon (see above example), the destruction of PCB was largely photolytic in nature.

SUMMARY

Because of the inherent advantages over the treatment alternatives, enhanced (advanced) oxidation processes will become the dominant method of treating groundwater contaminated with organic compounds in the future. This paper has discussed the **Rayox** second generation enhanced oxidation based water remediation system. Important features of the **Rayox** system have been discussed along with the results from many case studies which have demonstrated **Rayox's** ability to destroy a wide variety of pollutants in groundwater, including refractory compounds such as carbon tetrachloride, chloroform, dichloroethane and Freons, to any required discharge level. The results described here did not involve the use of ozone, thereby completely avoiding the requirement of any clean up of off gases containing ozone or VOC.

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FIGURE 1

POSTULATED DESTRUCTION MECHANISM FOR CHLOROFORM

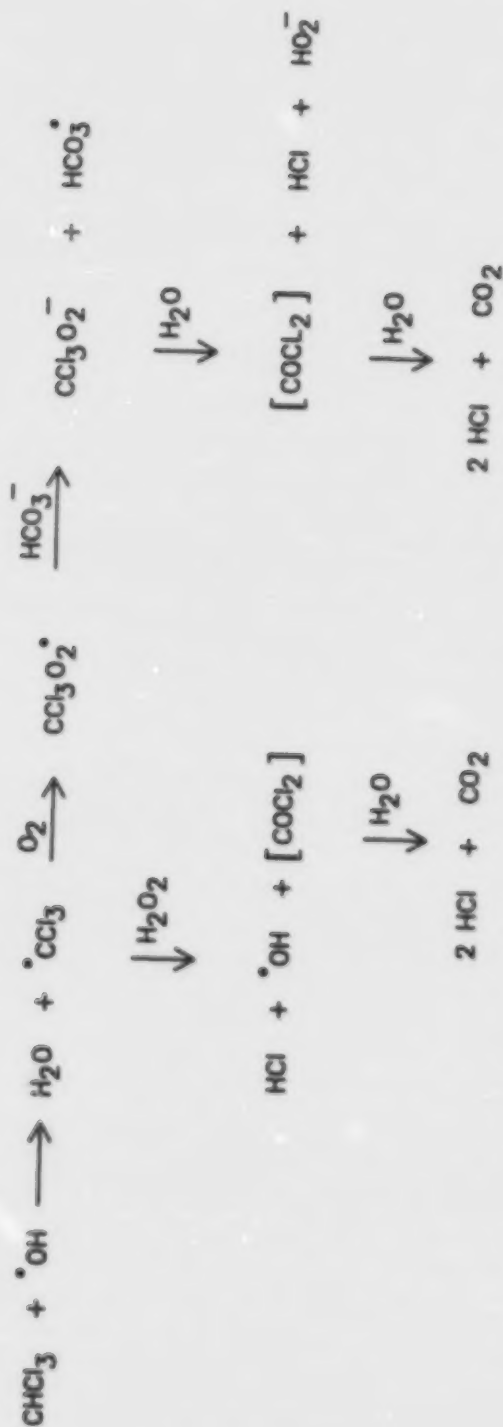


FIGURE 2

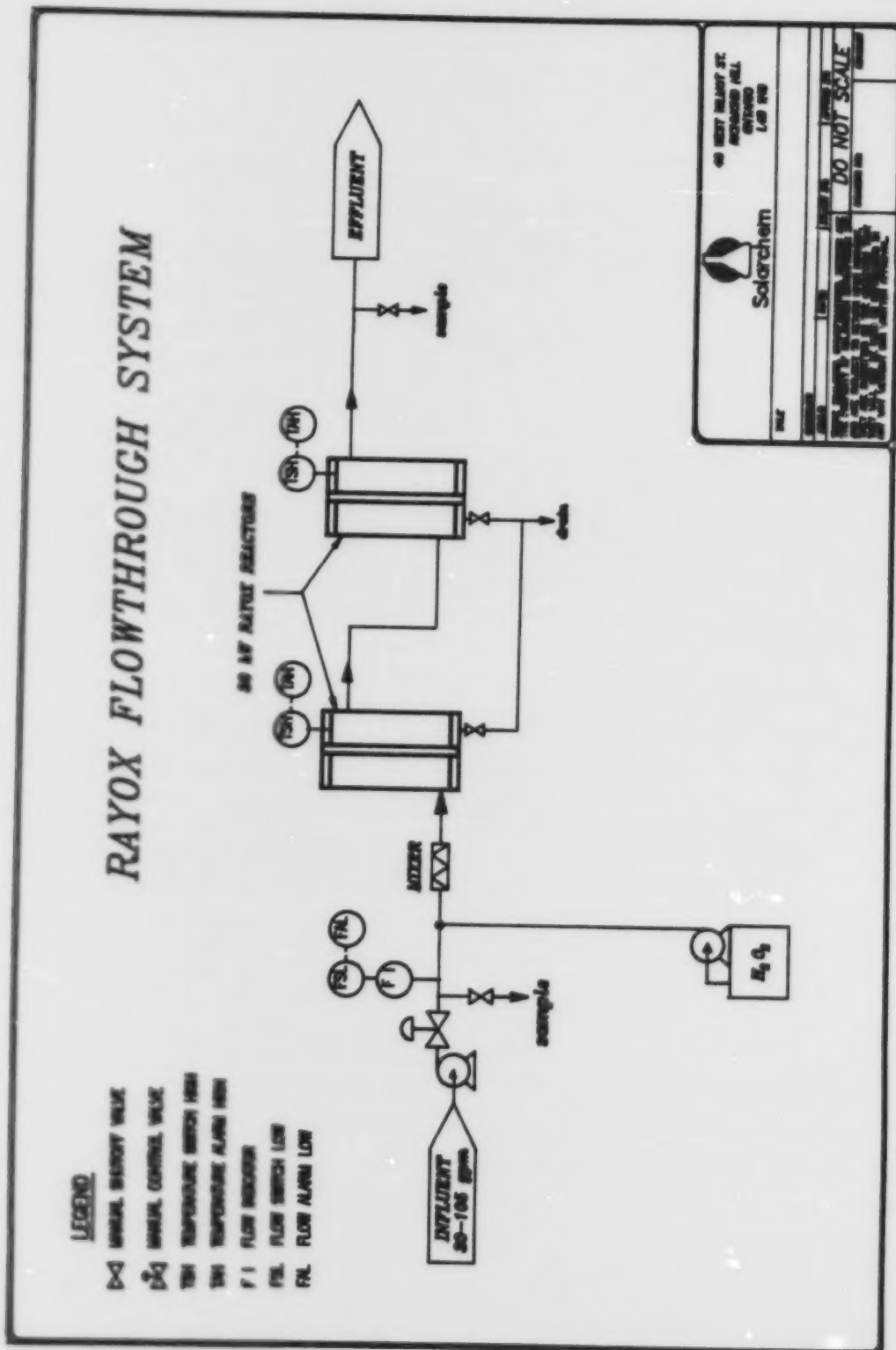


FIGURE 4

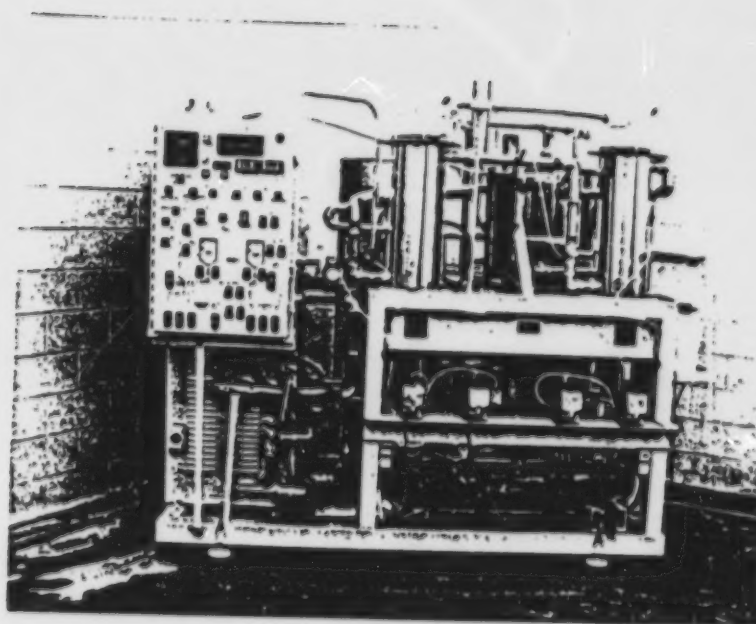


FIGURE 5

RAYOX DESTRUCTION OF NDMA IN CONTAMINATED DRINKING WATER

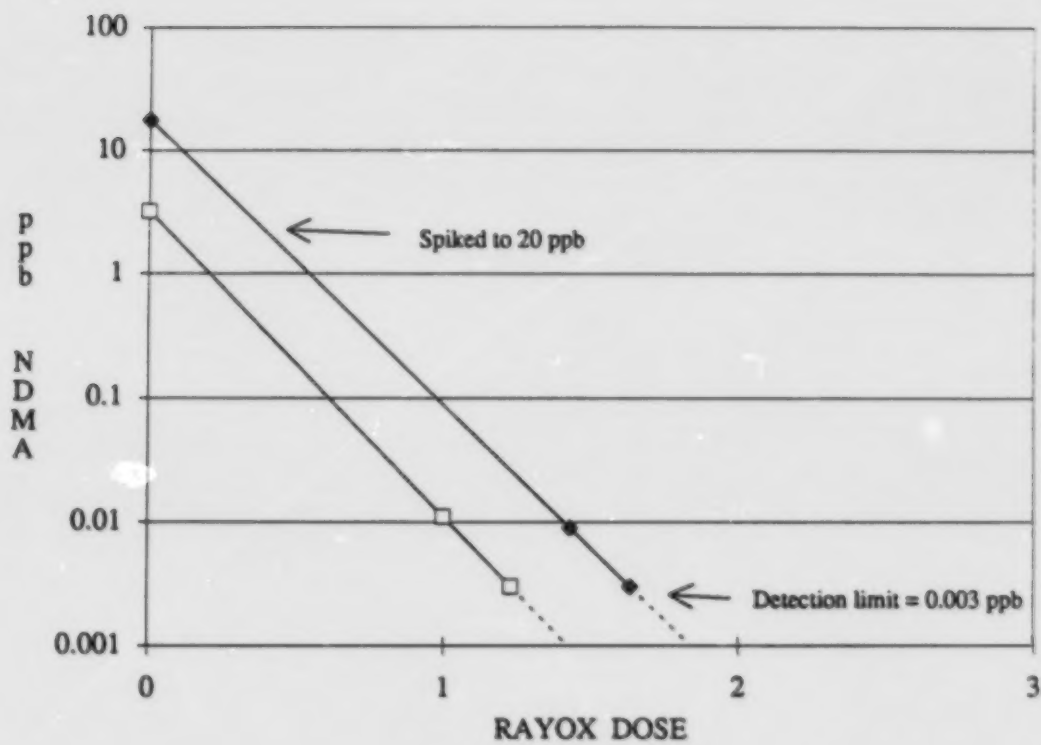


FIGURE 6

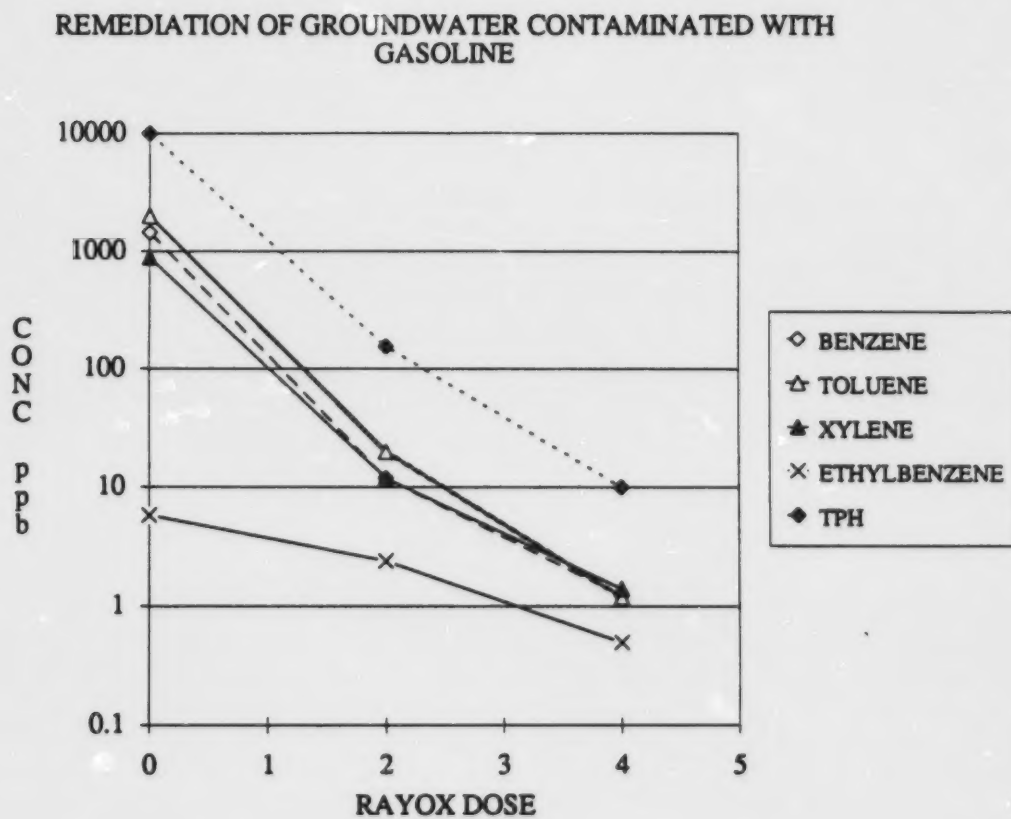


FIGURE 7

RAYOX TREATMENT OF 1,4-DIOXANE

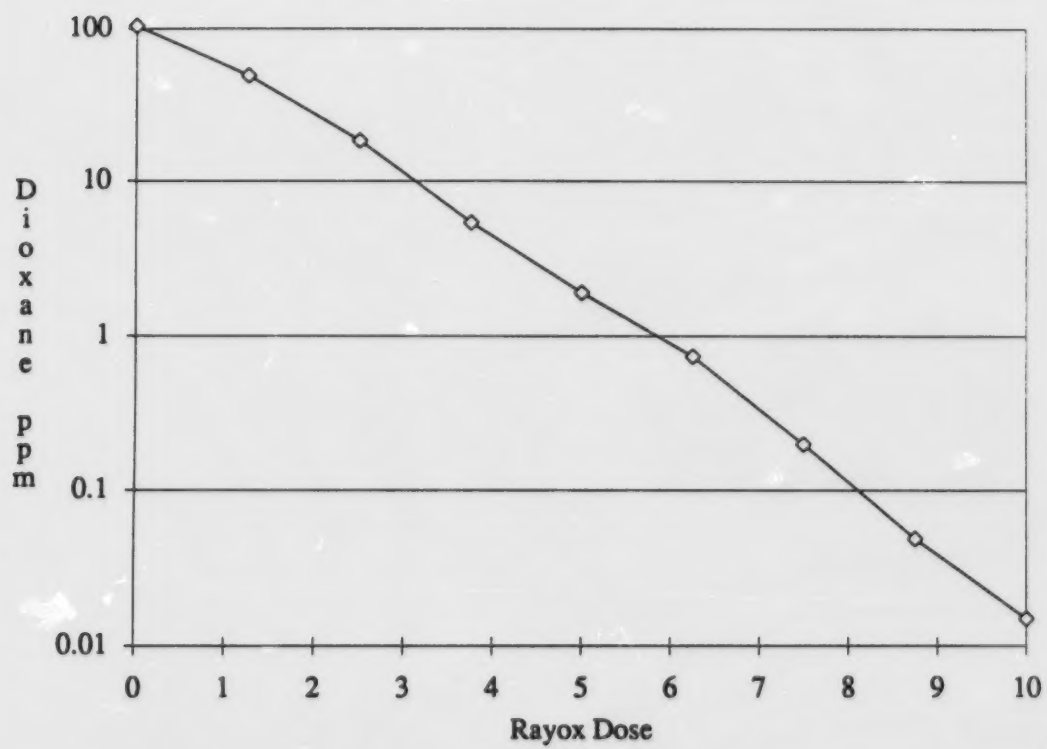
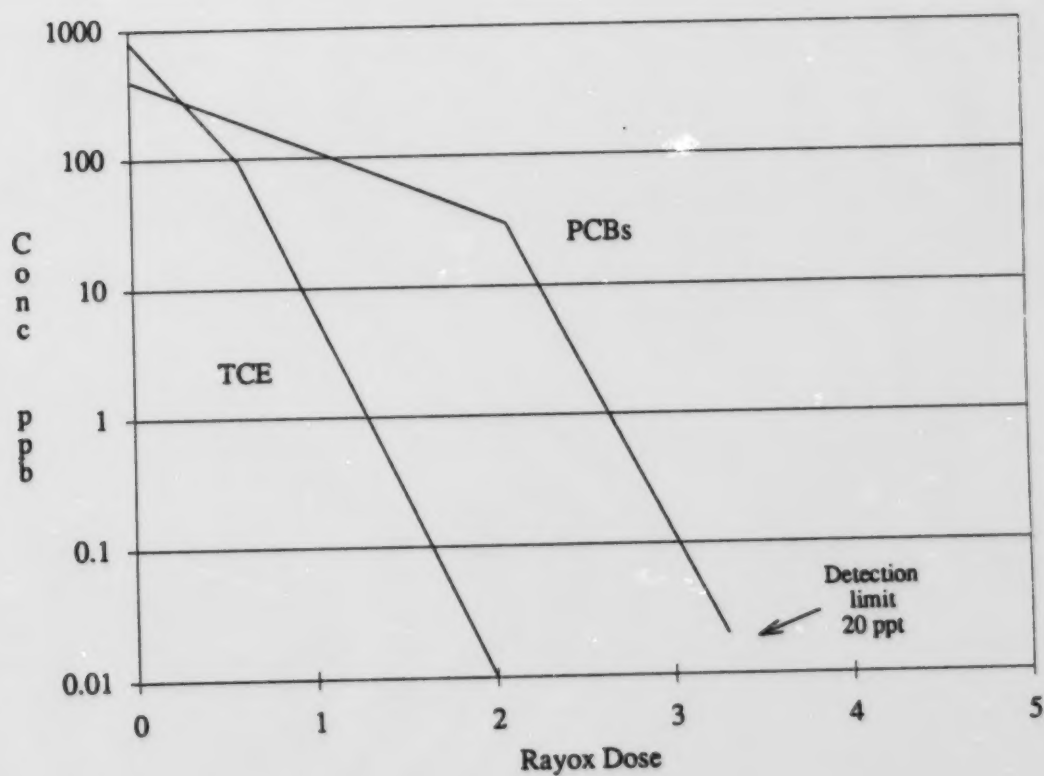


FIGURE 8

DESTRUCTION OF PCBs AND TCE IN GROUNDWATER





**THE perox-pure™ OXIDATION SYSTEM
A COMPARATIVE SUMMARY**

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ABSTRACT:

During the 1980's, the pollution control industry was pressed to reevaluate available technologies for removing organic contaminants from water and wastewater. This was especially true of "transfer" technologies such as stripping and adsorption that merely transfer the contaminant from one phase to another. In the 1990's "transfer" technologies will give way to more acceptable on-site destruction processes such as chemical oxidation.

This paper will present data from laboratory tests, field demonstrations and full-scale operating systems utilizing the perox-pure™ Treatment Process. In addition to economic and performance data, process improvements and advantages of this unique UV light catalyzed oxidation system will be highlighted. Comparisons to other advanced oxidation processes will include a discussion of basic process principals as well as equipment and operational considerations.

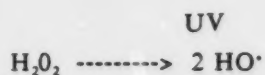
INTRODUCTION:

The development of the perox-pure™ UV peroxidation process was started in the late 1970's. Today, there are over thirty (30) full-scale treatment units that are in operation or in the final stages of design and installation, but the development and improvement of the process is continuing. This advanced oxidation process, using ultraviolet (UV) light catalyzed hydrogen peroxide has been shown to be a cost-effective treatment for a wide array of organic compounds found in contaminated groundwater, toxic waste leachates and industrial wastewaters. Recent improvements in the perox-pure™ Process have reduced the operating cost for total destruction of these toxic organics by up to 50%. In addition, the oxidation rate of many of the "difficult to oxidize" compounds such as 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), chloroform (CHCL₃) and methylene chloride (MeCl) have been increased up to three fold. These advances increase the cost effectiveness of on-site destruction

processes versus "transfer technologies" and broaden the applicability of chemical oxidation as the technology of choice.

perox-pure™ PROCESS

In this process, UV light converts the hydrogen peroxide (H_2O_2) in solution to hydroxyl radicals ($HO^\bullet$) and "activates" many of the organic molecules to make them easier to oxidize. The photolysis reaction which forms $HO^\bullet$ can be shown as follows:



The activation of the organic molecules can range from direct oxidation by absorption and disassociation to the formation of organic radicals or other reactive intermediates. With enough time and reactants, organic compounds can be completely destroyed to CO_2 , H_2O and, if present, the appropriate inorganic salt.

Most early UV oxidation processes used low pressure mercury vapor lamps combined with ozone (O_3). The perox-pure™ Process utilizes a proprietary high intensity UV lamp combined with H_2O_2 . This provides a number of advantages for chemical oxidation of aqueous solutions.

Three process considerations which manifest advantages include:

- o UV Intensity - The higher intensity allows for a more compact equipment design as well as lower capital cost. In addition, the higher UV intensity gives better penetration in wastewater or high concentration waters and allows for treatment of a wider range of applications.
- o UV Spectra - Since activation of organic compounds plays a key role in the destruction process, the broad spectra of the high intensity lamps is better suited for most applications than the narrow spectrum low pressure mercury lamps.
- o H_2O_2 - Because H_2O_2 is completely miscible with water, it can be easily added in any desired concentration. This wide range of concentrations combined with high intensity lamps allows for simplicity of reactor design, and short reaction times for both groundwater and wastewater applications. In addition, there are no toxic gas emissions or stripping of volatile organics into the air.

BENCH-SCALE TESTING:

Over the last five (5) years Peroxidation Systems, Inc. (PSI) has tested hundreds of water and wastewater samples from clients using bench-scale equipment. In addition, an on-going research and development program has contributed to the large body of information available on the oxidation of organic compounds by UV peroxidation. This data is stored in a computerized data base that can be used to generate preliminary process design and cost estimates for a given set of influent and effluent specifications. Table 1 is a partial listing of the compounds in the database.

Table 1
perox-pure™ Database
Organic Compounds Listing

Acenaphthene	Dichloropropene
Acenaphthylene	Dinitrophenol
Acetic Acid	Dieldrin
Acetone	EDTA
Acetonitrile	Endrin
Acrolein (Propenal)	Ethylbenzene
Acrylic Acid	Ethylene Diamine
Acrylonitrile	Fluoranthene
Alachlor	Fluorene
Alcohols	Formaldehyde
Aldicarb	Formic Acid
Aldrin	Hexachlorobenzene
Aniline	Hydrazines
Anthracene	Isophorone
Benzene	Methyl ethyl ketone (MEK)
Benzoic Acid	Methyl isobutyl ketone (MIBK)
Benzyl butyl phthalate	Methylene chloride
Bis (2-chloroisopropyl) ether	MTBE
Bis (2-ethylhexyl) phthalate	Napthalene
Bromodichloromethane	Nitroglycerine
Butyric Acid	Nitrophenol
Butyl Acrylate	Nitrosamine
Butylbenzene	PCBs
Carbon tetrachloride	Pentachlorophenol
Chloroaniline	Phenanthrene
Chlorobenzene	Phenol
Chlorodane	Tetrachloroethane
Chloroethane	Tetrachloroethene
Chloroform	Tetrahydrofuran
Chloromethane	Toluene
2-Chloronaphthalene	Trichlorobenzene
Chlorophenol	1,1,1-Trichloroethane
Cresol	1,1,2-Trichloroethane
Chlorotoluene	Trichloroethene
Cyanide	Trichlorofluoromethane
Cyclohexanone	2,4,6-Trichlorophenol
1,2-Dibromo-3- chloropropane	Trichlorophenols
Dibromochloromethane	Vinyl chloride
1,2-Dibromoethane	Xylene
Dichlorobenzene	
Dichlorobenzidine	
Dichlorodifluoromethane	
1,1-Dichloroethane	
1,2-Dichloroethane	
1,1-Dichloroethene	
1,2-Dichloroethene	
2,4-Dichlorophenol	
Dichloropropane	

Some of the important process variables affecting performance and costs are shown in Table 2.

Table 2
perox-pure™ Process Variables

- o UV and H₂O₂ Dosage
- o Reactor Design
- o Type and Concentration of Organics
- o Type and Concentration of Inorganics
- o pH
- o Catalyst

One of the unique differences of the perox-pure™ Process relates to the reactor design. Since most of the oxidation of organics occurs via a chemical reaction with hydroxyl radicals, the reactor is designed to optimize this process. A more detailed discussion of the benefits of perox-pure™ reactor design is presented under PROCESS IMPROVEMENTS.

Another advantage of the perox-pure™ design is the ability of the high intensity lamps to mitigate the negative effects of some inorganic compounds present in the water. There is significant data present in the literature indicating that alkalinity, due to bicarbonate ions, reduces the rate of HO· attack. The data shown in Figures 1-3 compare low pressure and high intensity lamps for oxidation of TCA and MeCl at different levels of alkalinity. Analysis of Figures 1 and 2, using low pressure lamps, illustrate that the oxidation rate for TCA or MeCl is about 6-10 times slower in Tucson, Arizona tap water or in distilled water with 200 mg/l alkalinity added than in distilled water only. This same lowering of oxidation rate is seen in Figure 3 using high intensity lamps, but the difference is less than two (2) times slower. A similar effect using low pressure lamps can be seen with easy to oxidize compounds such as TCE and benzene, but the negative effect is only 2-3 times slower. With high intensity lamps, no significant lowering is seen in tap water for TCE or benzene.

The overall effect of high intensity lamps combined with H₂O₂ is to provide for lower capital and maintenance costs, more flexibility in treating a broad range of organic compounds, and less problems with high concentrations of organics or interfering inorganic ions.

FULL-SCALE OXIDATION

Of the thirty (30) full-scale perox-pure™ systems in operation or final construction/installation, about 30% are treating wastewaters with organic concentrations

between 10 mg/l and about 1%. The remainder are treating groundwater. Table 3 shows a partial list of the organic compounds being treated by these installations. Operating costs for these treatment systems range from about \$0.50/1000 gallons for low concentration groundwater containing TCE and DCE to about \$0.12/gallon for the highest concentration wastewaters.

Table 3
perox-pure™ Operating Systems
Organic Chemicals List

Acrylic Acid	Ethyl Benzene
Aniline	Hydrazines
Benzene	Isopropanol
Bis 2-ethylhexyl phthalate	MeCl
Butyl Acrylate	PCE
Chlorinated phenols	Pentachlorophenol
Chlorobenzene	1,1,1-TCA
Chloroform	TCE
1,1-DCA	Total Toxic Organics
1,1-DCE	Vinyl Chloride
1,2-DCE	Xylene
Dimethyl Nitrosamine	

The following three examples illustrate the range of treatment achievable with the perox-pure™ Process. This first example shown in Table 4 uses a combination air stripper and perox-pure™ treatment system.

Table 4
Full-Scale perox-pure™ Treatment Data
Site 1

<u>Contaminant</u>	<u>Influent (µg/l)*</u>	<u>Effluent (µg/l)</u>
MeCl	1.0	BDL
1,1-DCA	5.0	BDL
1,2-DCE	187	BDL
1,1,1-TCA	116	65
TCE	71	BDL
PCE	272	BDL
Toluene	7	BDL

Residence Time: 2 min.

H₂O₂: 40 mg/l

* Effluent from Air Stripper.

While the treatment system performed well there was only partial removal of the difficult to oxidize TCA. In addition, the bulk of the volatile organics were being stripped into the air rather than being destroyed. Recently, the two treatment systems were reversed to evaluate the performance of the perox-pure™ unit on the more concentrated influent. The data shown in Table 5 is the average of samples taken over a three month period.

Table 5
Full-Scale perox-pure™ Treatment Data
Site 1 - Ahead of Air Stripper

<u>Contaminant</u>	<u>Influent (µg/l)</u>	<u>Effluent (µg/l)</u>	<u>Air Stripper (µg/l)</u>
MeCl	30	1.5	BDL
1,1-DCA	42	BDL	---
1,2-DCE	2466	BDL	---
1,1,1-TCA	1606	1218	<5
TCE	1060	BDL	---
PCE	3160	BDL	---

With about the same operating cost this treatment arrangement was able to destroy over 85% of the total volatiles, produce a cleaner effluent and eliminate about 90% of the air emissions. Operating cost for the perox-pure™ system is about \$2.00/1000 gallon.

The second example is a batch treatment operation on a concentrated wastewater containing hydrazines and other toxic organics. Table 6 shows typical results of the optimized treatment system.

Table 6
Full-Scale perox-pure™ Treatment Data
Site 2

<u>Contaminant</u>	<u>Influent (mg/l)</u>	<u>Effluent (µg/l)</u>
Hydrazine	1200	<1
Monomethyl Hydrazine	100	<10
Unsym. dimethyl Hydrazine	1500	<10
Nitrosodimethylamine	1.5	<0.02
Chlorinated Organics	75	<1
Pesticides/Herbicides	0.5	<1

While the operating cost for this extremely hazardous waste is high (\$0.12/gallon) in comparison to the other examples shown in this paper, it demonstrates the ability of the UV peroxidation process to handle concentrated wastes that can't be effectively or safely treated

by other technologies. Total on-site destruction of the toxic organics without any air emissions was one of the major factors in choosing the perox-pure™ system.

In this last example, the perox-pure™ treatment system is used to treat a high flow low concentration groundwater stream. The flow rate at this site ranges up to 400 gpm, with low $\mu\text{g/l}$ levels of TCE, 1,2-DCE and CHCl_3 present in the influent.

Table 7
Full-Scale perox-pure™ Treatment Data
Site 3

<u>Contaminant</u>	<u>Influent ($\mu\text{g/l}$)</u>	<u>Effluent ($\mu\text{g/l}$)</u>
1,2-DCE	6.2	BDL*
TCE	66.3	BDL
Chloroform	2.1	BDL

* BDL = $<0.1 \mu\text{g/l}$.

The operating cost for this site is about \$0.40/1000 gallons. Again, one of the main factors in choosing the perox-pure™ system was complete destruction of the organics with no by-products and no air emissions.

PROCESS IMPROVEMENTS

The perox-pure™ Process has proved to be a cost-effective treatment system for many groundwater and wastewater streams. On-going development work has focused on improving the process design with particular emphasis on the "difficult to oxidize" compounds such as 1,1,1-TCA, 1,1-DCA, MeCl and CHCl_3 . Recently, Peroxidation Systems, Inc. (PSI) announced a significant breakthrough that can reduce the operating cost for the perox-pure™ process by 30-50%. This new proprietary design is incorporated in all new equipment and can be retrofitted to existing perox-pure™ equipment. While the details of this new second generation design will not be presented in this paper, it is important to note that the improvement comes from advances in both reactor design and electrical/lamp system performance.

The improvement in oxidation rate of some selected compounds is shown on bench-scale equipment in Figures 4-6. This data was generated using spiked tap water solutions containing mixtures of 3-5 volatile organic chemicals at an initial total organic concentration of 5-15 mg/l . In all cases the oxidation rate increased by 2-3 times with the new B design. Similar

testing done on clients groundwater and wastewater samples show the same range of oxidation rate improvement with these "difficult to oxidize" chemicals.

Although only limited full-scale operational data is available with the new design, Tables 8 and 9 show two examples of the cost reduction and/or performance increase achieved.

Table 8
Full-Scale perox-pure™ Treatment Data
Old vs New (B) Design
Site 4

Contaminant	Inf. (µg/l)	Eff. (µg/l)	Operating Cost (\$/1000 gal)*	
			Old	New
TCE	8.4	<0.001	\$ 1.22	---
	11.1	<0.001	---	\$0.54
1,1,1-TCA	0.1	<0.02	14.58	---
	0.15	<0.03	---	3.86

* Costs based on \$0.07/KWH and \$0.50/lb. H₂O₂ as 50%.

Note that there was a significant cost reduction for TCE removal as well as TCA.

Table 9
Full-Scale perox-pure™ Treatment Data
Old vs New (B) Design
Site 5

Contaminant	Influent (µg/l)	Effluent (µg/l)	
		Old	New
MeCl	600-800	245	33
1,1,1-TCA	200-400	145	26
1,2-DCE	50-250	<1	<1

The effluent requirements for Site were lowered to meet new discharge standards. By retrofitting the new design to the existing unit, the new effluent standards were met with no increase in cost.

SUMMARY

In the 1990's "transfer technologies" will give way to more acceptable on-site destruction processes such as chemical oxidation. The **perox-pure™** Oxidation System has proven to be a cost-effective treatment process for the on-site destruction of toxic organic chemicals in groundwater and wastewater. Continuing improvements in the technology and costs will enable the **perox-pure™** Process to be one of the technologies of choice for the 1990's.

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FIGURE 1

LOW PRESSURE LAMP
TCA OXIDATION
UV/H₂O₂

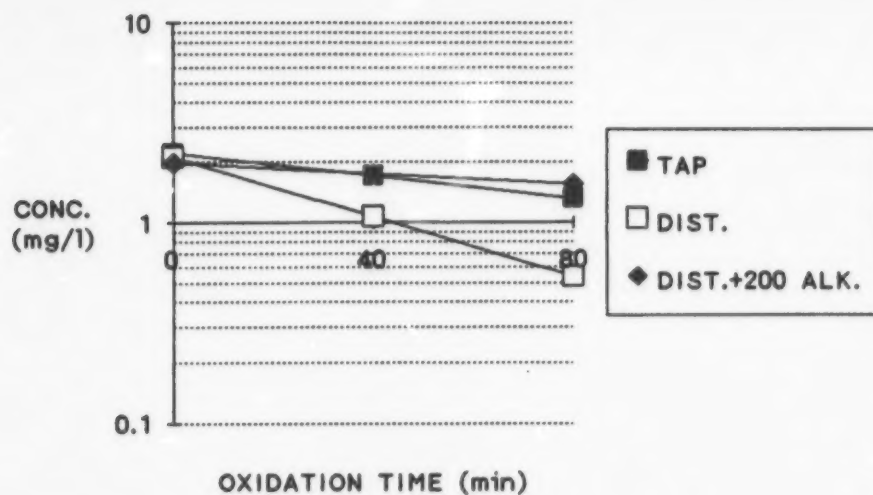


FIGURE 2

LOW PRESSURE LAMP
MeCl OXIDATION
UV/H₂O₂

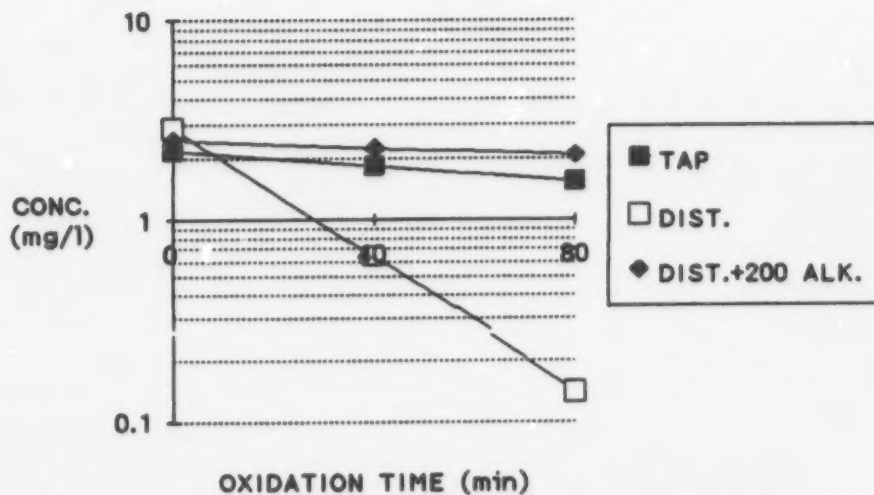


FIGURE 3

HIGH INTENSITY LAMP
UV/H₂O₂

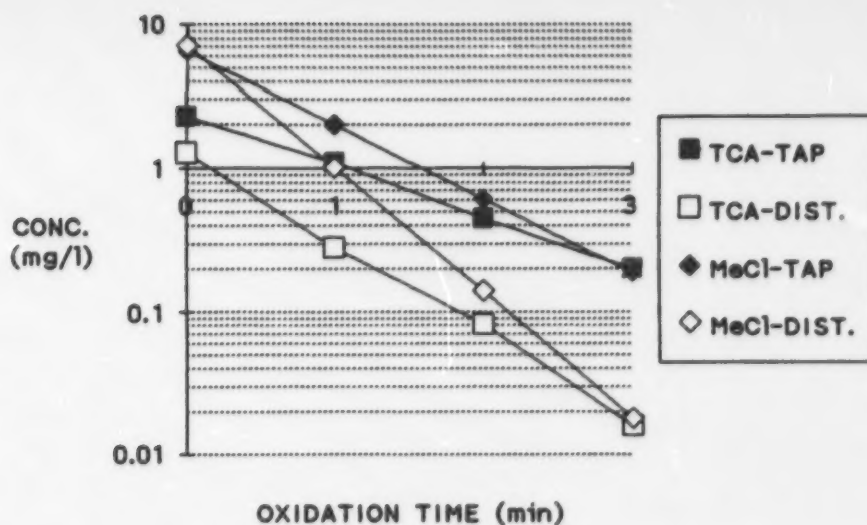


FIGURE 4

BENCH-SCALE PEROX-PURE TESTS
OLD vs NEW (B) DESIGN

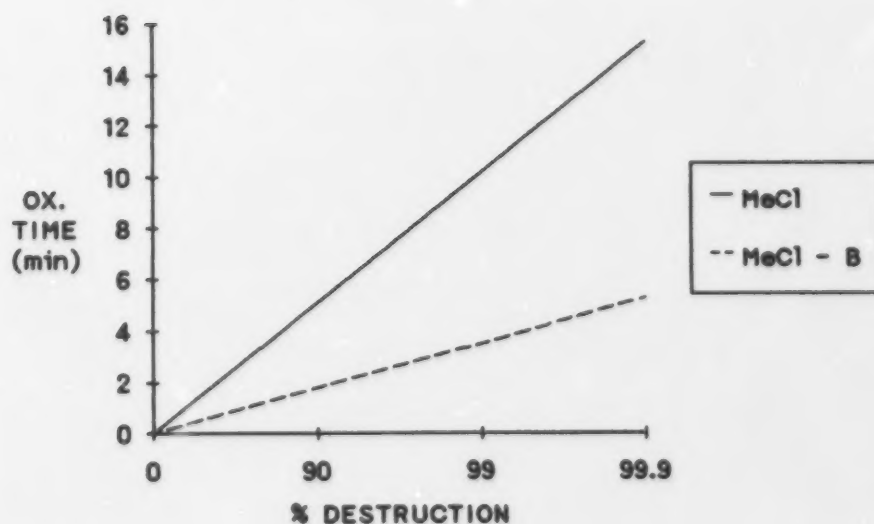


FIGURE 5

BENCH-SCALE PEROX-PURE TESTS
OLD vs NEW (B) DESIGN

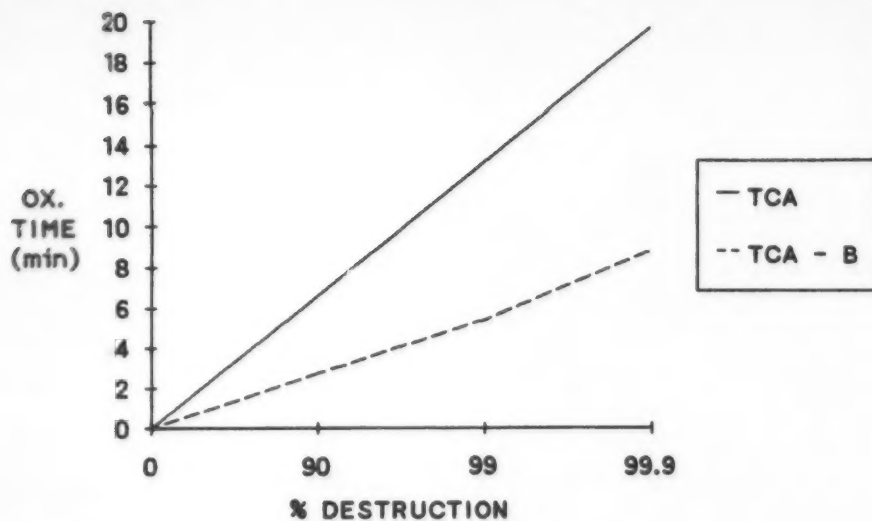
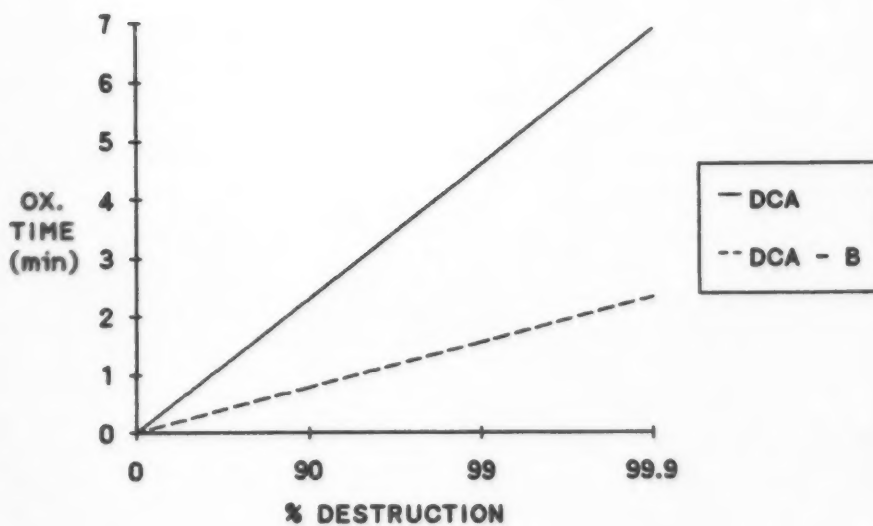


FIGURE 6

BENCH-SCALE PEROX-PURE TESTS
OLD vs NEW (B) DESIGN



**THE UVOX PROCESS
APPLIED TO REDUCTION OF TRIHALOMETHANE
FORMATION POTENTIAL AND DISINFECTION**

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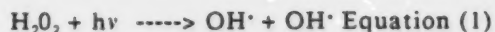
ABSTRACT

The UVOX process was developed to reduce the high concentrations of trihalomethanes (THMs), a potentially hazardous disinfection by-product (DBP), found in a surface water supply for a community in northeastern Saskatchewan. Pilot plant tests were conducted at a throughput of 75 litres per minute utilizing UV to produce $\text{OH}^\cdot$ radicals from photolysis of H_2O_2 utilizing air cooled UV units. These tests continued through 1985, 1986 and 1987 to provide operational data for all seasons of the year. Test results indicated that the UVOX process was effective in reducing THM formation potential (THMFP) to very low levels. Recent concerns have also centred on the biocidal effectiveness of disinfectants particularly when applied to inactivation of resistant species of microorganisms, such as the cysts of *Giardia lamblia*. The UVOX process enhanced the ability of UV to inactivate *Giardia* cysts. A research protocol was described which would increase the efficiency of the UVOX process for disinfection purposes.

PART 1: TRIHALOMETHANE FORMATION POTENTIAL REDUCTION

INTRODUCTION: ADVANCED OXIDATION PROCESSES

There have been continuing developments in the field of advanced oxidation processes (AOPs) since the 1970's. These developments include work on combinations of UV plus ozone, UV plus hydrogen peroxide (H_2O_2), and more recently ozone (O_3) and H_2O_2 . The most direct method, and in principle, the method which should give the highest yield of $\text{OH}^\cdot$ radicals, is direct photolysis of H_2O_2 . Photolysis of H_2O_2 is believed to yield $\text{OH}^\cdot$ radicals, with a quantum yield of two $\text{OH}^\cdot$ radicals formed per quantum of radiation absorbed (Baxendale & Wilson, 1957):



Where, $h\nu$ = Moles of Photons (Einsteins) from UV Irradiation.

The molar extinction coefficient of H_2O_2 at 254 nm is only $19.6 \text{ M}^{-1}\text{s}^{-1}$ ($\text{Moles}^{-1} \times \text{seconds}^{-1}$) which is exceptionally low for a primary absorber in a photochemical process (Baxendale and Wilson, 1957). The value for ozone is $3\,300 \text{ M}^{-1}\text{s}^{-1}$. This means that in order to generate an equal concentration of $\text{OH}^\cdot$ radicals through UV photolysis there must be a higher concentration of H_2O_2 , as compared to O_3 , in the medium [Glaze *et al*, 1987(b)].

A literature search traced the origin of advanced oxidation processes back 50 years (Bray, 1938), when the interaction between ozone and hydrogen peroxide in aqueous solution was first identified. Taube and Bray collaborated in describing chain reactions in aqueous solutions containing O_3 , H_2O_2 and acid (Taube and Bray, 1940). The first article on photochemical reactions of O_3 in solution appeared later (Taube, 1957). Subsequent work concentrated on photochemical reactions, after the discovery that a new intermediate entity, identified as the hydroxyl radical ($\text{OH}^\cdot$) generated by photolysis of O_3 and H_2O_2 , was responsible for the increased oxidation activity of O_3 (Hoigné and Bader, 1975). The postulation of the existence of $\text{OH}^\cdot$ radicals dates from much earlier research (Weiss, 1935). Recognition that H_2O_2 could assist in ozonation of organic compounds in water prompted additional work [Hoigné and Bader, 1978, 1983(a) and (b); Nakayama *et al*, 1979; Staehelin & Hoigné, 1982, 1985; Glaze, 1987; Glaze *et al*, 1987(a) and (b)].

The results for THMFP reduction by the UVOX process at 1.25 L/s pilot scale (Jansson, 1988) indicate that THMFP from a highly enriched surface water supply could be reduced to less than $20 \mu\text{g/L}$ at an operating cost of \$0.20/1000 Imperial gallons.

Oxidation of taste and odor (TAO) compounds was carried out at bench scale with nine oxidants on both Colorado River water (CRW) and State Project water (SPW) at UCLA (Glaze *et al*, 1988). These studies concluded that conventional oxidants such as chlorine, chloramines, chlorine dioxide, potassium permanganate and hydrogen peroxide would not be able to control the TAO problems in water supplies due to geosmin and 2-methylisoborneol (MIB). MIB was the most refractory to oxidation of the two TAO compounds used in the study. Advanced oxidation processes generating highly reactive $\text{OH}^\cdot$ radicals were more successful than conventional oxidants in TAO compound destruction. Ozone alone was found to satisfactorily oxidize MIB, probably because the water contained natural constituents that reacted with ozone to form $\text{OH}^\cdot$ radicals.

Concerns about AOPs that generate $\text{OH}^\bullet$ radicals, are effectiveness, cost and the possible side effects. Such side effects may include the formation of by-products with undesirable health effects. In the pilot scale studies conducted for MWDSC it was indicated that 0.01 to 0.12 mg/L residuals of H_2O_2 remain in the water after the peroxone process and for ozonation alone (McGuire and Davis, 1988). It was hoped that the peroxone process optimization might reduce these residuals to undetectable levels in treatment plant effluents. The questions of toxicology and carcinogenicity of H_2O_2 were briefly reviewed for Los Angeles Department of Water and Power. (Bull, 1988). Bull suggests that no serious hazard would be encountered at a threshold concentration of H_2O_2 of <6 mg/L as a result of drinking water treatment. This observation was based on several factors; that there is only limited evidence of H_2O_2 carcinogenic activity; the magnitude of endogenous formation of H_2O_2 could be compared to the amount that would be obtained from drinking water; the activity of H_2O_2 as a carcinogen probably depends upon its conversion to $\text{OH}^\bullet$ radicals. It was noted that in biological systems the conversion of exogenous or endogenous H_2O_2 to $\text{OH}^\bullet$ radicals depends on the availability of free iron. This means that carcinogenicity of H_2O_2 could only be expressed after sufficient cell damage by H_2O_2 has occurred to make noncomplexed iron available for formation of $\text{OH}^\bullet$ radicals. Should the threshold level of H_2O_2 of <6 mg/L threshold level suggested by Bull be accepted, the possibility of utilizing H_2O_2 as a residual disinfectant in water distribution systems, replacing free chlorine and chloramines, becomes a possibility. This should uncover additional fruitful areas for research and development, including the use of AOPs as disinfection processes for resistant microorganisms such as *Giardia*, followed by a non-chlorine based residual disinfectant (Jansson, 1988).

PRELIMINARY STUDIES:

The Saskatchewan Department of Environment commenced testing for trihalomethanes (THMs) for the municipal water supply of Melfort, Saskatchewan (population 6 000) in May, 1980. Two samples were tested, one in May and one in June, which exceeded the Canadian Guidelines for Drinking Water Quality (Minister of Health & Welfare, 1978) of 350 $\mu\text{g/L}$ Total THMs (TTHMs), with one sample exceeding 500 $\mu\text{g/L}$. The existence of the high TTHM levels indicated that an alternative to prechlorination should be investigated.

The work of Michael Pereira (U.S. EPA, Cincinnati), (Hileman, 1982) discussed the mechanism by which THMs induce cancer and explained the distinction between initiators and promoters of cancer, with the conclusion that THMs were considered to be promoters of cancer.

During 1981 a study was instigated to evaluate several common pretreatment alternatives, potassium permanganate, chlorine dioxide and ozone (Jansson, 1982). While the use of ozone in combination with ultraviolet light (UV) was known to the study group (Glaze *et al*, 1980), it was found that ozone would be too expensive to implement on a full scale basis for a small community that did not have experienced personnel capable of operational efficiencies. Data from the tests on the three pre-oxidants revealed that these alternative would not economically reduce THMs. The use of powdered activated carbon as a replacement for prechlorination (Anderson *et al*, 1980) was attempted by the plant operators, but the concentration of microorganisms increased to a level that caused rapid filter plugging.

The author was familiar through personal contacts with the researchers at NIVA (the Norwegian Institute for Water Research), Oslo, into the use of ultraviolet irradiation in combination with H_2O_2 for the reduction of naturally occurring humic substances (Gjessing & Goodmunson Rogne, 1982). Studies on the use of UV plus H_2O_2 for total organic carbon (TOC) reduction and disinfection were also reported in the North American literature (Legan, 1982).

In September, 1983 Jansson Consulting conducted a series of tests, funded by a Regina manufacturer of water conditioning equipment, using UV plus H_2O_2 pretreatment of water from the highly organic Buffalo Pound lake supply of Regina and Moose Jaw. A single pass system was designed, where H_2O_2 was injected prior to a UV unit, Model 40H (Ultraviolet Technology Inc., Sacramento, CA). The information obtained indicated that a single pass system would probably not be feasible because a certain minimum reaction time was necessary for THM precursors to be oxidized. As was typical with UV disinfection units, water was only retained in the UV unit for a few seconds.

Using information from the single pass trials a small recirculation loop was built at the Regina manufacturing plant, consisting of the Model 40H UV unit, chemical feed pump for H_2O_2 addition, a recirculation pump and an open 60 litre polyethylene tank reservoir. Several tests were conducted in which TOC was the parameter used to test for reduction in organic matter, an indicator of lowered levels of THMFP, according to work with UV plus O_3 in East Texas - Louisiana (Glaze *et al*, 1987, Peyton *et al*, 1987). The tests on Melfort water did not result in lowering of TOC concentrations, contrary to tests by NIVA and Glaze, Peyton *et al*. Neither did subsequent tests on Buffalo Pound raw water. A sample of the Melfort water was submitted to the Provincial Health Laboratory, in which 35 mg/L of free chlorine was added, incubated for 8 days at room temperature, and tested for THMFP utilizing gas chromatography (GC). The Sample contained 897 $\mu\text{g/L}$ TTHM prior to UVOX treatment. After recirculation through the UV unit with dosage of 40 mg/L H_2O_2 for 120 minutes, the

TTHM was found to be less than 50 µg/L. The results were reported in Figure 1. The TOC level only decreased from 14 to 12. A mass spectrograph (MS) was taken of the untreated and treated samples, and while the peaks for the treated sample were truncated, the MS was more complex than that of the untreated sample. This appeared to indicate that although approximately the same concentration of TOC was present, it was now composed of many more compounds at lower concentrations.

INITIAL PILOT PLANT OPERATION:

A 75 litre per minute (20 US gpm) pilot plant was designed by Jansson Consulting, constructed by Water Conditioning Group Inc., and housed within a 10 by 40 foot trailer. It was moved to Melfort in 1985.

In October, 1985, batch tests with recirculation through the UV units, similar to those carried out at small scale in October, 1983 were performed with the pilot plant. The batch tests of October, 1985 indicated substantial THMFP reduction, as shown in Figures 2 and 3. The TOC was virtually constant and, therefore, refractory to UVOX destruction, although there probably was a rearranging of the chemical nature of the TOC matrix, as suggested by the 1983 batch test GC-MS analyses.

Initial pilot plant tests conducted in September, 1985 revealed inconclusive results with continuous flow, the intended mode of operation. Following an evaluation of the procedures these initial test results were thought to have been unsatisfactory, not because the system was unsatisfactory for continuous flow, but because the samples obtained were refrigerated at 5°C, and stored on site for a few days prior to removal of the samples to the laboratory. The variation in results between the September, 1985 continuous flow tests and the October, 1983 and 1985 batch tests confirmed this phenomenon. The new procedures mandated that the samples must be put on ice, transported directly to the laboratory and chlorinated within hours of the test run, as this would simulate actual plant practice, chlorination immediately after UVOX treatment. This adjustment in test protocol completed the standardization of procedures for the 1986 continuous flow testing program.

TESTING AND ANALYTICAL PROCEDURES:

Pilot plant procedures involved starting the raw water pump in the non-chlorinated wet wall, switching on and adjusting the UV pretreatment unit. The booster pump which forced water through a 0.9m diameter pressure sand filter was activated and filtered water was transferred

to the pilot plant. The filter was backwashed with chlorinated water treatment plant effluent prior to each test run, and had to be flushed out with raw unchlorinated water prior to changing the valve status to transfer filtered water to the pilot plant. As the pilot plant the flow was adjusted to 75 litres per minute (20 US gpm), valves were opened or closed to allow sequential flow through tanks 1, 2 and 3, and the effluent pump was started to return pilot plant effluent to the water treatment plant clarifier, where it mixed into the main plant flow. Since tanks 1 and 2 were designed for 30 minutes nominal retention, it took about an hour for the filtered water to flow to the aeration tower, tank 3. Once flow reached tank 3, it was elevated to the top and then was allowed to free fall by gravity through a polyethylene flow dividing media against a countercurrent air flow of 600 scfm. When the effluent reached the aeration tank bottom, it flowed by gravity to the effluent pump for transfer back to the water treatment plant. The recirculation rates for tanks 1 and 2 were established by the number of UV units chosen for the particular test run. Each unit was rated at 150 litres per minute (40 US gpm), therefore, if 5 UV units were utilized, the recirculation rate was 750 litres per minute (200 US gpm). Hydrogen peroxide was measured into 10 litre plastic water jugs, and the chemical feed pump, which had been precalibrated, was adjusted to deliver the required flow for a test run, at say 20 mg/L H_2O_2 . The H_2O_2 was supplied in 20 gallon opaque black polyethylene containers at 35 per cent by volume strength (Prairie Industrial Chemicals Ltd., Saskatoon, SK). All flow measuring devices were of the direct reading impeller type, designed for flow measurement error of +/- one per cent (Brian Engineering, Winnipeg, MB).

Analysis for THMs was accomplished by a Hewlett Packard 5730A Gas Chromatograph equipped with a SPB-5 column, 30m x 0.75mm, and an electron capture detector [Hewlett-Packard (Canada) Ltd, Toronto, ON]. Analytical procedures were in accordance with the American Society for Testing and Materials methodology for solvent extraction gas chromatography, ASTM Method D3973. Color and odor were analyzed according to Standard Methods for the Examination of Water and Wastewater (Standard Methods, 1980). Color was reported in APHA units, while odor was reported as a (dilution) number.

Some of the July and August, 1986 test runs were discarded due to a malfunctioning chemical feed pump. This was subsequently mitigated by estimating H_2O_2 solution flow rate, and confirming it by marking the solution level in the semitransparent polyethylene 10 litre jugs prior to the start of a test run and at test run completion, and then calculating the actual solution flow. After the samples were in the laboratory, incubation and analysis required a two week wait before results were known. Because the budget was limited, it was generally decided not to proceed with the next set of tests before results from the previous test runs were known.

TEST RESULTS AND DISCUSSION OF RESULTS:

The results on tests without H_2O_2 in the incoming flow revealed no reduction of THMFP after 225 minutes of operation. The samples were taken from the tank 2 exit; 10 UV units were operated in the two tank sequence, 5 for each tank. In late October, 1985 THMFP had dropped to 172 in the filtered water, but in accordance with previous data, there was no reduction in THMFP unless both UV and H_2O_2 were used.

With a concentration of 10 mg/L H_2O_2 and with 5 UV units, the decrease in THMFP was not significant in water with an APHA level of 34. As water temperature cooled color in the raw water changed to amber from an algae green. With 25 mg/L H_2O_2 , THMFP was lowered from 172 to 81 $\mu\text{g/L}$ in a 100 minute batch test. On November 6, 1985, 90 minutes of recirculation utilizing 5 UV units and 25 mg/L H_2O_2 reduced THMFP from 284 to 103 $\mu\text{g/L}$, with most of the decrease occurring within 15 minutes. The raw water color had increased, and now registered 37 APHA units. In Figure 4, results were shown separately for chloroform (CFM) and dichlorobromomethane (DCBM), and it was noted that while CFM decreased by 68 per cent from 220 to 70 $\mu\text{g/L}$, DCBM only decreased by 48 per cent from 64 to 33 $\mu\text{g/L}$, indicating that the precursors for DCBM are more resistant to oxidation by UVOX than CFM precursors. Additional analyses for dibromochloromethane (DBCM) and bromoforms (BFMs) confirmed that these were minor components of TTHMs.

Batch tests conducted on November 7, 1985, indicated that 2 mg/L H_2O_2 and 5 UV units reduced THMFP from 284 to 154 $\mu\text{g/L}$, a reduction of 46 per cent in 115 minutes of recirculation. With the addition of 10 mg/L to a subsequent batch test of the same day, utilizing 5 UV units, plus the cooling air from 10 UV units (five each from tanks 1 and 2) bubbled into tank 1, the THMFP reduction dropped to 28 per cent. While these results appeared to be contradictory, it was suspected that the vigorous mixing from the cooling air caused excessive volatilization of H_2O_2 . During winter 1985-86 the cooling air diffusers were modified into fine bubble (sock) type to eliminate this problem.

Tests on April 25, 1986, again indicated that without H_2O_2 , UV would have no effect on THMFP reduction, and that the cooling air from 10 UV units did not contain enough ozone (derived from action of the UV lamps on the oxygen in the cooling air) to have an effect on THMFP. The aeration process of tank 3 also did not have any effect on reduction of THMFP.

Tests conducted May 9, 1986 on a continuous flow basis at 75 litres per minute indicated that H_2O_2 without UV had no effect in reduction of THMFP, but that when 5 UV units were used

within the tank 2 recirculation loop, THMFP dropped from 100 to 52 $\mu\text{g/L}$, as shown in Figure 5. As also shown in Figure 13, it was found that 12 mg/L H_2O_2 in tank 1 reduced THMFP from 100 to 71, and THMFP continued to drop through tank 2, to 32 $\mu\text{g/L}$. At low H_2O_2 concentrations, it appeared that more complete THMFP reduction would require longer than 30 minutes retention.

The May 30, 1986 tests were conducted with 12 mg/L H_2O_2 , with only 2 UV units in the recirculation loops of tanks 1 and 2 through tank 3, the aeration tower. This series was repeated under the same conditions with 4 UV units in the recirculation loops, and while the results following flow through tanks 1 to 3 were similar, there was more consistent THMFP reduction in the flow from tank 1 to 2 and 3. With 4 UV units in the recirculation loops of tanks 1 and 2, there was a smoother curve, indicating more consistent THMFP reduction as more UV irradiation was applied.

The results from three test runs of July 23, 1986 were scheduled so that a reduction of the number of UV units in the recirculation loops was combined increased retention (decreased flow rate), so that the same amount of UV irradiation would occur for each test, but the test time would be extended respectively from 30 minutes per tank to 60 and 120 minutes. The chemical feed pump malfunction had reduced the intended 25 mg/L H_2O_2 to 14 mg/L, but it was confirmed that no more than 30 minutes retention was needed. Less than 30 minute retention was not possible, because the hydraulic capacity of the pilot plant was 75 litres/minute, allowing for a minimum detention time of 30 minutes in tank 1 and 2.

On June 25, 1986 the pilot plant was operated utilizing effluent from the Melfort water treatment plant (WTP). This effluent had been prechlorinated at a rate of 5 mg/L and post chlorinated at 5 mg/L. The raw water pH was consistently in the 8.3 to 8.5 range. Only 8 mg/L H_2O_2 was utilized due to the chemical feed pump problem during that period, but the UVOX process was still effective. With 2 UV units in the tank 1 recirculation loop, and 4 UV units for tank 2, THMFP was lowered from 56 $\mu\text{g/L}$ in the WTP effluent, to 48 after tank 1 and 39 after tank 2. The reason for UVOX process reduced THMFP in chlorinated WTP effluent was postulated to be the time required for THMs to develop in this water. To test this hypothesis samples were taken July 23, 1986 from raw filtered effluent water (the pilot plant supply) and from WTP effluent, pre and post chlorinated respectively at 4 and 3 mg/L. These samples were incubated with 35 mg/L chlorine for 1, 4 and 8 days. At the end of these incubation times the samples were analyzed for TTHMs. The results of these tests are reported in Table 1.

TABLE 1 DEVELOPMENT OF THMs IN MELFORT WATER

Days of Incubation	THMs in Sample ($\mu\text{g/L}$)	
	Raw Filtered Water	WTP Effluent
1	12	12
4	270	250
8	290	260

The data of Table 1 indicate that it would be possible to reduce THMFP in both prechlorinated and postchlorinated WTP effluent as THMs develop over a period of time. Only a fraction of the THMs developed in the first 24 hours. Most of the remainder of THMFP was developed over a 4 day period. In the succeeding 4 days of the 8 day incubation, little additional THMFP was expressed.

Tests confirming the above results, reported in Figure 6, were conducted September 10, 1986, after the chemical feed pump problems had been mitigated. With 20 mg/L H_2O_2 and 4 UV units in the tank 1 and 2 recirculation loops, THMFP of 212 $\mu\text{g/L}$ was reduced to 4 in tank 1 with 30 minutes retention, and was reduced to 5 after tank 2. Color remained equal at 35 APHA units, however, but odor was reduced from 8 for the filtered raw water, to 3 after tank 2. The reduction appeared to be caused by aeration of tank 2 with cooling air from 8 UV units. A parallel test was performed September 12, 1986 with Melfort WTP effluent, with pre and post chlorine doses of 3 mg/L, and reported in Figure 7. Approximately the same results were achieved with 30 mg/L H_2O_2 , with continued reductions through tank 2. Color was virtually unchanged, while odor at 3 units, was identical to the previous test. In Figure 8, the September 12, 1986 results for conditions similar to those of Figure 7 were reported, except that half as many UV units were utilized in Tank 1. Tests with 30 mg/L H_2O_2 and 4 UV units each for tanks 1 and 2, were performed September 11, 1986, with virtually the same results, as indicated for the 20 mg/L H_2O_2 tests of Figure 6. Additional tests later in September with 40 mg/L H_2O_2 yielded less THMFP reduction, indicating excessive oxidation of the organic matrix. Also, tests with 10 mg/L H_2O_2 were not as effective as the earlier tests with 20 and 30 mg/L H_2O_2 . The reason was probably due to too low a concentration of H_2O_2 to effectively provide enough $\text{OH}^\cdot$ radicals to oxidize the THM precursors.

OBSERVATIONS:

The focus of water treatment researchers and operators has been directed towards the replacement of free chlorine with alternative disinfectants, since formation of THMs (and other chlorinated by-products) from the chlorination of organically enriched waters, was recognized as a potential health hazard. The use of ozone, or ozone in combination with UV, has been extensively studied as a means to achieve potable water without employing chlorine.

Ozone, an unstable compound compared to chlorine, cannot provide a residual in storage and distribution systems to prevent regrowth of harmful microorganisms. In contrast hydrogen peroxide is stable in water, degrading by only 1 per cent per year in pure water, provided that it is not exposed to ultraviolet irradiation, either from UV units or from incident light. Without UV irradiation and with concentrations of up to 25 mg/L H_2O_2 , precursors to THM formation were minimally affected. When combined with UV in the UVOX process, H_2O_2 is capable of preventing the formation of significant concentrations of TTHMs in previously chlorinated water, provided that contact with chlorine is restricted to a day or less, so that THMs have not been formed prior to UVOX treatment.

Glaze *et al* carried out studies in a continuously stirred batch reactor with feed rate of 10 mg of H_2O_2 per minute to break down trichloroethylene (TCE). The TCE was decomposed at a reasonable rate, but the H_2O_2 residual gradually increased to 2.0 mg/L. In the UVOX pilot plant studies, H_2O_2 was introduced at a known test concentration, but the continuous recirculation at 4 to 10 times the flow rate through the UV units should decompose the H_2O_2 . A test apparatus to measure H_2O_2 residual (Lazarus *et al*, 1985) was not available at the Melfort pilot plant during the study, due to cost constraints, although the desirability of this information was recognized.

UVOX was operated as a tertiary treatment process, after much of the particulate matter and some of the turbidity was removed by means of filtration. The tertiary configuration is only one option for UVOX. Because UVOX is an oxidative as well as a photolytic process (Prengle, 1977), with potential for disinfection of water, it could be more effectively utilized as a pretreatment process, replacing prechlorination. The residual forming characteristics of H_2O_2 should be evaluated for residual disinfection purposes, if risk assessment indicates that some residual is acceptable.

The other potential application of UVOX is for wastewater disinfection. Because the combination of UV irradiation and H_2O_2 did not lower TOC in this heavily organically enriched water, UVOX may not dissipate its effects in side reactions and therefore be cost effective. It would be interesting to test UVOX as a disinfectant for secondary wastewater effluent in both single pass and recirculation modes.

CONCLUSIONS:

The data presented herein support the following conclusions:

- The UVOX process significantly reduced THMFP.
- Precursors to CFM were more readily oxidized than those for DCBM, DBCM or BFM.
- In the Melfort case, the precursors for THMs were not primarily derived from humic materials imported into the raw water reservoir through snowmelt inflow, but appeared to be generated within the reservoir through the growth and decay of algae species. Colored waters from forested and muskeg areas did not immediately lead to high THMFP in the spring, and when the reservoir water cooled in the autumn followed by algae dieoff, THMFP again decreased. THMFP was at its peak in late summer after the supply of nitrogen in the reservoir had been exhausted, and the predominant algal species were blue green algae that could directly utilize atmospheric nitrogen. The THMFP levels were at their highest during very warm summers, when blue green algae predominate. THMs from algae were also reported in the literature.(Oliver & Schindler, 1980). For example in 1983, after a warm summer, THMFP levels remained as high as 897 $\mu\text{g/L}$ in October.
- It was demonstrated that UVOX should successfully reduce THMFP in highly organic waters prechlorinated for one day or less. The costs for UVOX operation would be somewhat higher for prechlorinated water.
- An alternative to prechlorination would be the utilization of UVOX as a pretreatment process.
- UVOX might be applied as a pretreatment process, followed by post treatment with H_2O_2 as a residual disinfectant, if a small hydrogen peroxide residual in drinking water is acceptable.

- The estimated cost for operation of a UVOX plant in the highly enriched water, based on unoptimized pilot plant results, for a 1 to 2 MGD facility is 20 cents (Canadian) per 1 000 US gallons. This estimate is based on 5 months of UVOX operation with an average of 20 mg/L H_2O_2 , and year round operation of the UV system (Jansson, 1988).

PART 2: GIARDIA MURIS CYST INACTIVATION WITH THE UVOX PROCESS:

GENERAL:

The definitive study to date utilizing ultraviolet radiation (UV) for inactivation of *G. muris* was completed at the University of Washington in 1985 (Carlson *et al*, 1985). A detailed review of the fundamentals of UV disinfection were also presented in their report, which was prepared for the Water Engineering Research Laboratory (WERL), US EPA, Cincinnati, OH.

Changes have occurred in the manufacture of UV units, since circa 1984. The low pressure, mild glass shell UV lamp has to a large extent been replaced by a higher intensity lamp with a quartz glass shell. Mild glass shells reduced the frequency of UV irradiation from 254 to about 239-240 nanometers (nm), ($nm = 10^{-9}m$), at which frequencies UV has the ability to create ozone from the oxygen in air or dissolved oxygen in water. Because the quartz glass shell does not lower UV frequency the medium intensity lamps are virtually ozone free (Petrowich, 1987). The median life of the the newer lamp is about 10 000 hours, slightly longer than the former standard of 7-8 000 hours.

The application of alternative disinfectants was also summarized in Environmental Science and Technology (Hileman, 1982). It was noted by Richard Bull, Toxicologist with U.S. EPA, Cincinnati, OH; that all commonly used forms of disinfectants alter the composition of trace organic chemicals because the efficacy of disinfectants "depends on their ability to alter organic chemicals by either chemical or physical means."

UVOX DISINFECTION TESTS:

Test protocols for the operation of the UV unit, Universal Water Systems Inc., Model NPS #3, Serial No. 1029 (Universal Water Systems Inc., Vancouver, B.C.), were established prior to initiating tests with UV and UV/H₂O₂ to inactivate *G. muris* cysts. The step by step procedure that was followed is given below:

- The test reservoir was filled with distilled/demineralized water and the reservoir was coupled to the pump intake. The reservoir was mounted on a separate caster trolley, so that it could be wheeled to the distilled water supply. A schematic illustration of the test apparatus is given in Figure 9.
- The main pump was started and the flow rate was adjusted to 0.1 liters per second (L/s) utilizing the direct reading flow meter, Cal Q Flo, Model CF-300 (Blue White Industries, Westminster, CA). The pump was a Jacuzzi, Model EP 500 S1/A (Jacuzzi, Canada Ltd., Mississauga, ON).
- The UV unit was switched on and was allowed to warm up to a stable radiation level. The stability of output was noted when the Amarco intensity gauge needle indicated constant output. The intensity gauge was calibrated in millivolts (mv), not in UV dosage units of micro watt seconds per centimeter squared (μ ws/cm²). The UV unit is shown in Figure 10.
- The H₂O₂ solution was mixed, so that by means of the calibrated output of the chemical feed pump (CFP), the H₂O₂ concentration would be diluted to 10, 20, or 30 mg/L in the flow through the UV unit as required by the test protocol. The CFP utilized in the tests was an Ebara, Model EP-B25 (Chem-Tech International/Iwaki, Lowell, MA).
- After the flow was stabilized, 500,000 cysts were injected directly into the cyst port through a rubber membrane seal with a hypodermic syringe. At the 0.1 L/s flow rate, cysts would begin exiting the test unit 15 seconds after injection, and would continue to flow until 36 seconds into the test. The CFP would be switched on for 25 seconds prior to cyst injection to stabilize H₂O₂ concentration.
- The CFP and main pump would be allowed to operate for an additional 65 seconds to flush all cysts and peroxide out of the test unit.

To minimize corrosion, all surfaces in contact with water or test solutions were non-ferrous, because oxides of iron are strong UV light absorbers. Materials utilized included copper, bronze, stainless steel, polyvinylchloride (PVC), and polyethylene.

To establish the actual UV dosages to which the *G. muris* cysts were exposed, the Amaro intensity meter was recalibrated from mv units to UV intensity units. Recalibration of the intensity meter was carried out by the addition of Bentonite, an inorganic clay (Avonlea Minerals Ltd., Avonlea, SK) to the distilled/demineralized water to create turbidity. The turbidity was measured by a Hach Turbidimeter Model 2100A (Hach Chemical Co., Ames, IA). Absorption of UV light at 254 nm was measured using Standard Methods (Standard Methods 15th Edition, 1980). Absorption at 254 nm was matched with the UV unit manufacturers measurements of UV intensity for water with transmissibility of 86 per cent at full scale of the Amaro intensity meter. The fluid mechanics of the UV unit was analyzed so that UV exposure times in seconds for the two flow rates could be accurately estimated. The UV dosage was then calculated by combining the two parameters, intensity and exposure time and relating these to the manufacturer's measured dosage at 14 per cent absorbance, a full scale reading on the Amaro intensity meter. After the match point was established a range of turbidities was used to recalibrate the intensity meter scale in $\mu\text{Ws}/\text{cm}^2$ units.

To provide field data for UVOX application some tests were conducted with algae and bacteria, microorganisms that would be encountered in field conditions. A mixed culture of algae was supplied by the Regina Water Research Institute of the University of Regina (RWRI), to provide organic matter and turbidity. The cells of the mixed algae culture, greens and blue-greens, were not counted but their effect on UV intensity could be ascertained from the UV intensity monitor readings. Another microorganism, a pseudomonad bacterium, was drawn from an RWRI culture used to break down bacterial plugs that form in water wells. The pseudomonad contains the enzyme, catalase+, that is able to rapidly oxidize H_2O_2 to its constituents, water and oxygen. Consequently the organism is referred to as "catalase". "Catalase" was used in a concentration of 250,000 colony forming units per ml (CFU).

The UVOX tests reported herein were conducted at 0.1 L/s with concentrations of 10, 20 and 30 mg/L H_2O_2 and two "blank" samples, one with UV and without H_2O_2 and one with H_2O_2 only, for each test set. Similar tests were carried out with algae and "catalase". Concentration of cysts for the larger volume test samples, which generated 3 to 4 litres, was accomplished using 500 ml centrifuge flasks in the first stage, then reverting to 15 ml centrifuge tubes for succeeding steps.

When cysts are inactivated by means of a chemical oxidant diffusing through the protective membrane layers, the cyst was inactivated by damage to the vital tissue of the cell. It was concluded in a study on the effects of chlorine on cyst ultrastructure (Neuwirth *et al*, 1988) that chlorine damage occurs at the cellular level even before the damage is manifested in morphological changes to the cell. The cyst can appear normal under electron microscopy but this does not necessarily mean that the cell is viable. Consequently, in the induction phase of excystation the cyst will not "bud" if it is non viable. Budded cysts are counted as two viable trophozoites in chlorine inactivation studies.

For UV inactivation, however, the cell damage was not apparent. Inactivation with UV occurred as a result of the formation of pyrimidine dimers between links in the deoxyribonucleic acid (DNA) that carries the code for cell replication and other vital processes (Venosa, 1983; Schenck, 1979). The interposing of the dimers breaks the DNA molecule into inoperative segments, destroying the viability of the cell, and the cell dies. Large membrane bound ectoplasmic vacuoles are seen in cysts prior to the induction phase of excystation. After induction these ectoplasmic vacuoles appear to dump their contents into the peritrophic space, the space between the cell wall and the cell ectoplasm. It was speculated that the contents of these vacuoles was enzymatic (Schaefer, 1987; Coggins and Schaefer, 1986) which was supported by evidence that these vacuoles contained lysosomal enzymes (Feely, 1982; Lindmark, 1980). More conclusive evidence was recently found (Feely and Dyer, 1987) who demonstrated acid phosphatase activity in the ectoplasmic (peripheral) vacuoles of *G. muris* and *G. lamblia* cysts. The UV irradiation does not prevent these enzymatic processes from occurring in induced cells. Consequently, a high proportion of cysts in UV tests were "budded", which under microscopic examination appeared as a partial state of excystment. These "budded" cysts never fully excysted, although sometimes the flagella could be seen in motion. The UV inactivated cysts, "budded" and intact, darken after UV contact. Due to the different process of UV inactivation, "budded" cysts were counted as non-viable, whereas they are counted as two viable trophozoites in chlorine inactivation tests.

TEST RESULTS:

Each bar graph shown for the UVOX experiments represents the results of a test. The common data base for all points was the "blank" which was used to normalize the test results.

TEST DATA:

According to the information in Figure 11, the UVOX process decreased cyst survival from 10.3 per cent with UV alone to 7.9 per cent with 10 mg/L H_2O_2 . The UV dosage utilized was 140,000 $\mu\text{ws}/\text{cm}^2$, which resulted from a flow rate of 0.1 L/s, with a reading of 1.0 mv on the UV intensity monitor.

With an increased H_2O_2 concentration of 20 mg/L, there was essentially no change in UVOX effectiveness, as indicated in Figure 12. For 30 mg/L H_2O_2 , however, UVOX decreased cyst viability to 6.8 per cent, as noted in Figure 13.

In each of the three tests there should be sufficient concentration of H_2O_2 to generate sufficient $OH^\cdot$ radicals. The limiting factor in this study was probably reaction time, because the degree of inactivation of the *G. muris* cysts was almost constant for the 10, 20 and 30 mg/L concentrations of H_2O_2 used in the test series.

With a mixed algae culture providing some turbidity and color, the UVOX process, with 20 mg/L H_2O_2 reduced cyst viability to 15.3 per cent from 20.2 per cent with UV alone. The intensity monitor reading was lowered to 0.88, which reduced the UV dosage from 140,000 to 139,000 $\mu\text{ws}/\text{cm}^2$, as shown in Figure 14.

The results from tests utilizing a bacteria culture that contained an enzyme capable of rapidly breaking down H_2O_2 , or "catalase" tests, were interesting. These series of tests were conducted later on the same day, with the same cyst stock as the algae tests. The algae test "blank" excysted at 88 per cent, while the "catalase" blank excysted at 88.6 percent, which was a good test of the consistency of the excystment technique. The intensity monitor reading was also 0.88 for the "catalase" tests, because of a slight color generated in the water distillation system. The UV dosage was 139,000 $\mu\text{ws}/\text{cm}^2$, identical to that used in the mixed algae culture tests.

The first "catalase" test was conducted with UVOX at 10 mg/L H_2O_2 . The results were surprising, as the cyst viability was very low, only 0.85 per cent, for the first test with utilization of 10 mg/L H_2O_2 . The percentage viability actually increased to 5.1 per cent for a subsequent test at 20 mg/L H_2O_2 . These results are reported in Figure 15.

The second set of "catalase" tests were conducted with the "catalase" containing bacteria mixed into the reservoir, where they were allowed to contact the peroxide for 15 minutes prior to UV irradiation. The 10 mg/L H_2O_2 "catalase" results are given in Figure 16. The Figure 16

results compared with the catalase pretreated data of Figure 15, also with 10 mg/L H_2O_2 , show that cyst viability increased from 0.85 per cent to 2.5 per cent. For the 20 mg/L H_2O_2 test of Figures 15 and 16, a similar comparison indicated that cyst viability decreased from 5.1 per cent to 3.9 per cent.

The "catalase" tests were complex. The microorganisms introduced, while overwhelmingly "catalase" were not purified, so that there were many possibilities for unexpected results. Many replications would have been required to ensure reproducible results, which was beyond the scope and financial support for this preliminary investigation. The best technical explanation for the low viabilities produced in the "catalase" tests, however, is that rapid breakdown of H_2O_2 by the catalase+ enzyme resulted in the release of singlet oxygen, or other short lived, highly reactive species including $OH^\cdot$ radicals, in addition to $OH^\cdot$ radicals produced by photolysis of H_2O_2 . While $OH^\cdot$ radicals are short lived, they considerably amplify the oxidation and presumably also the biocidal potential of H_2O_2 . The oxidizing potential, volts, of some common oxidants is: chlorine, 0.54; chlorine dioxide, 1.57; hydrogen peroxide, 1.78; ozone, 2.07; hydroxyl radical, 2.80; fluorine, 3.03. The creation of $OH^\cdot$ radicals from photolysis of H_2O_2 increases the oxidation potential by more than 57 per cent. Only fluorine has a higher oxidation potential than the $OH^\cdot$ radical.

The decrease in the inactivation rate when the "catalase" bacteria were mixed into the reservoir for 15 minutes prior to the test was probably the result of lower concentration of catalase+ enzyme in the solution when it passed through the UV unit. When the "catalase" bacteria were injected along with the *G. muris* cysts in the first set of tests, the "catalase" enzyme would not have been depleted with side reactions prior to the test, but would have been available for photolysis of H_2O_2 into $OH^\cdot$ radicals when irradiated with UV photons.

CONCLUSIONS:

The preliminary studies with the UVOX process applied to disinfection provide tentative conclusions:

- The low molar extinction rate for H_2O_2 exposed to UV at a wavelength of 254 nm was probably not a factor in the lower than expected rates of inactivation of *G. muris* cysts in the tests with UVOX at 10, 20 and 30 mg/L H_2O_2 concentration. There was virtually no change in inactivation among all three concentrations of H_2O_2 . It was postulated this effect was due to insufficient exposure time.

- There was a larger decrease in inactivation from the mixed algae culture than was apparent from the small decrease in dosage registered on the UV intensity monitor. There was probably some "UV demand" created by the addition of organic matter in the form of algae which needed to be satisfied before inactivation of *G. muris* cysts could take place. The concept of "UV demand" was introduced in the University of Washington studies on UV inactivation of *G. muris* cysts (Carlson *et al*, 1985).
- The addition of bacteria with the ability to release an enzyme, catalase+, capable of rapidly breaking down H_2O_2 is also likely to initiate generation of $OH^\cdot$ radicals. This is believed to be the reason for the unexpectedly high inactivation rates reported for the "catalase" tests.
- The test data for UVOX on *G. muris* cyst inactivation were sufficiently positive to warrant further investigation. Studies with longer contact times for UV/ H_2O_2 , similar to the successful UVOX pilot plant tests for THMFP reduction, could be used to develop UVOX into mature technology for inactivation of resistant microorganisms like Giardia and Cryptosporidium.
- Additional studies should be conducted with UVOX, applied to disinfection, to establish the kinetics and dynamics of the process. There is a requirement for new instrumentation to observe the creation and decay of $OH^\cdot$ radicals. With a knowledge of the experimental environment for maximization of $OH^\cdot$ radical generation, new equipment could be designed for UV/ H_2O_2 disinfection processes that could routinely meet objectives for 99.9% disinfection of resistant microorganisms.
- Existing UVOX pilot plant equipment could be utilized to conduct recirculation studies, resulting in more effective UV contact times for inactivation of resistant microorganisms, such as *Giardia* cysts and *Cryptosporidium* oocysts. The pilot plant test methodology described in Part I could be adapted as a model for additional disinfection trials.

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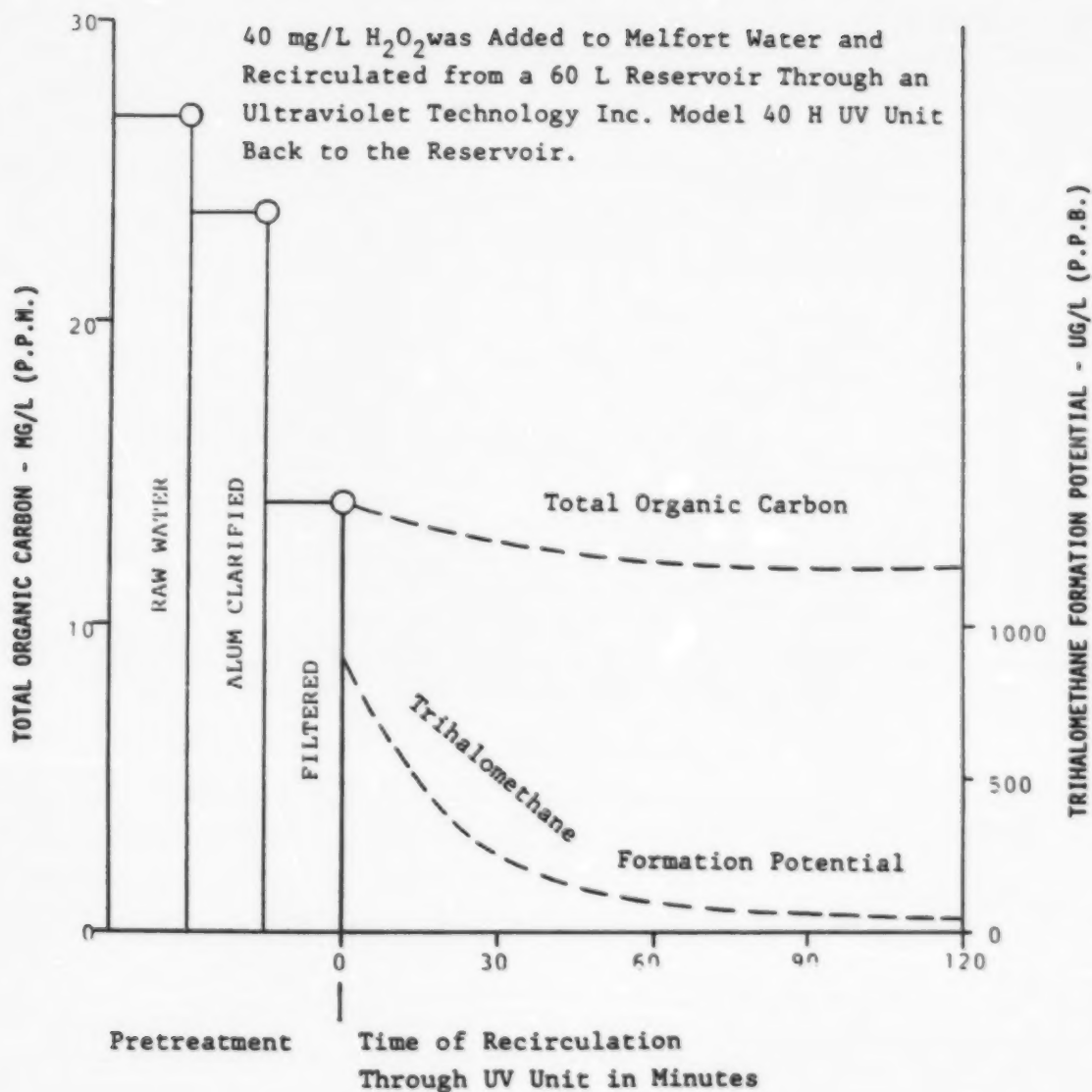


FIGURE 1: Total Organic Carbon and Trihalomethane Formation Potential Reduction in Small Scale UV Plus Hydrogen Peroxide Test.

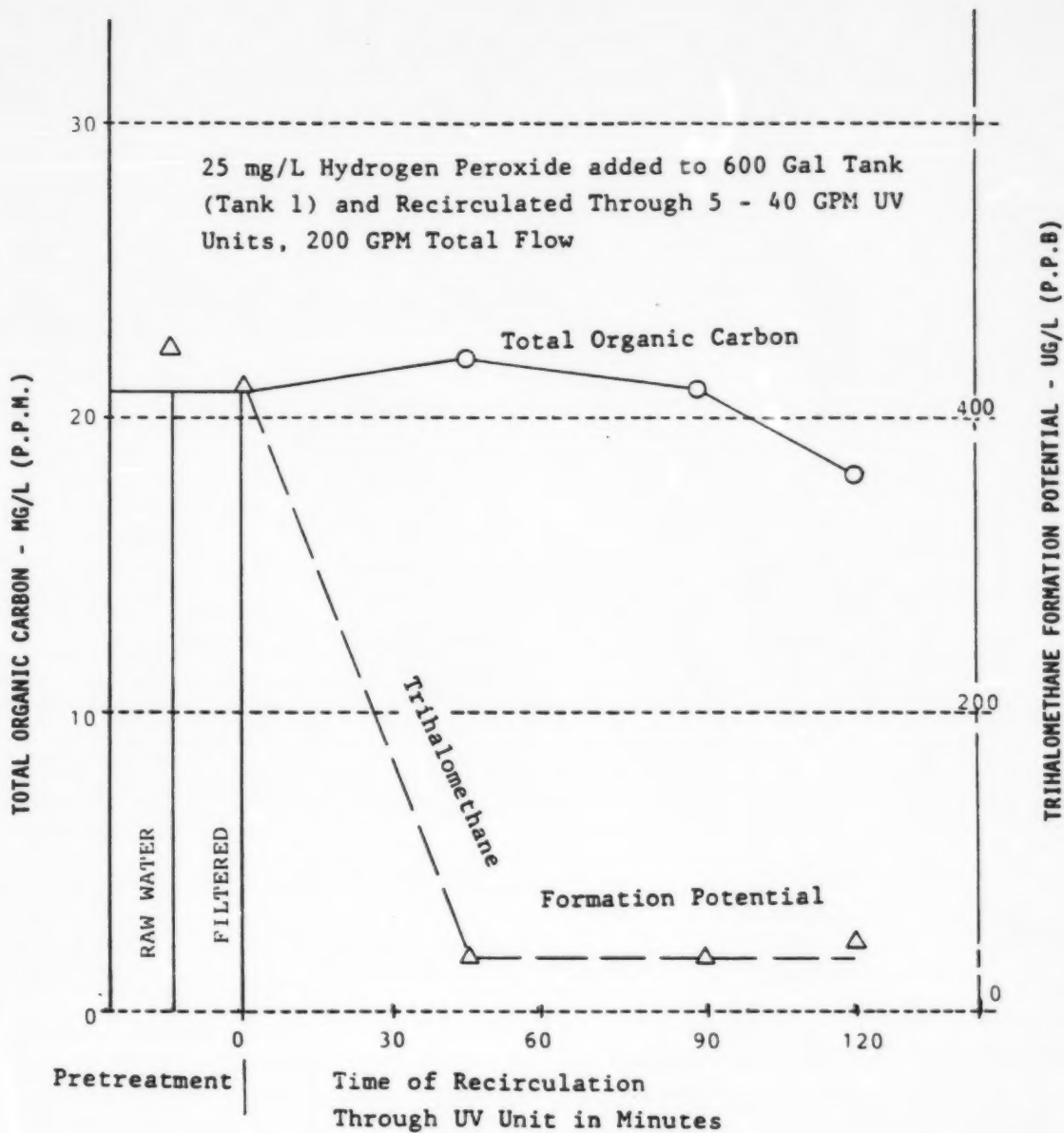


FIGURE 2: Pilot Plant Batch Test of Total Organic Carbon and Trihalomethane Formation Potential Reduction with UV Plus Hydrogen Peroxide.

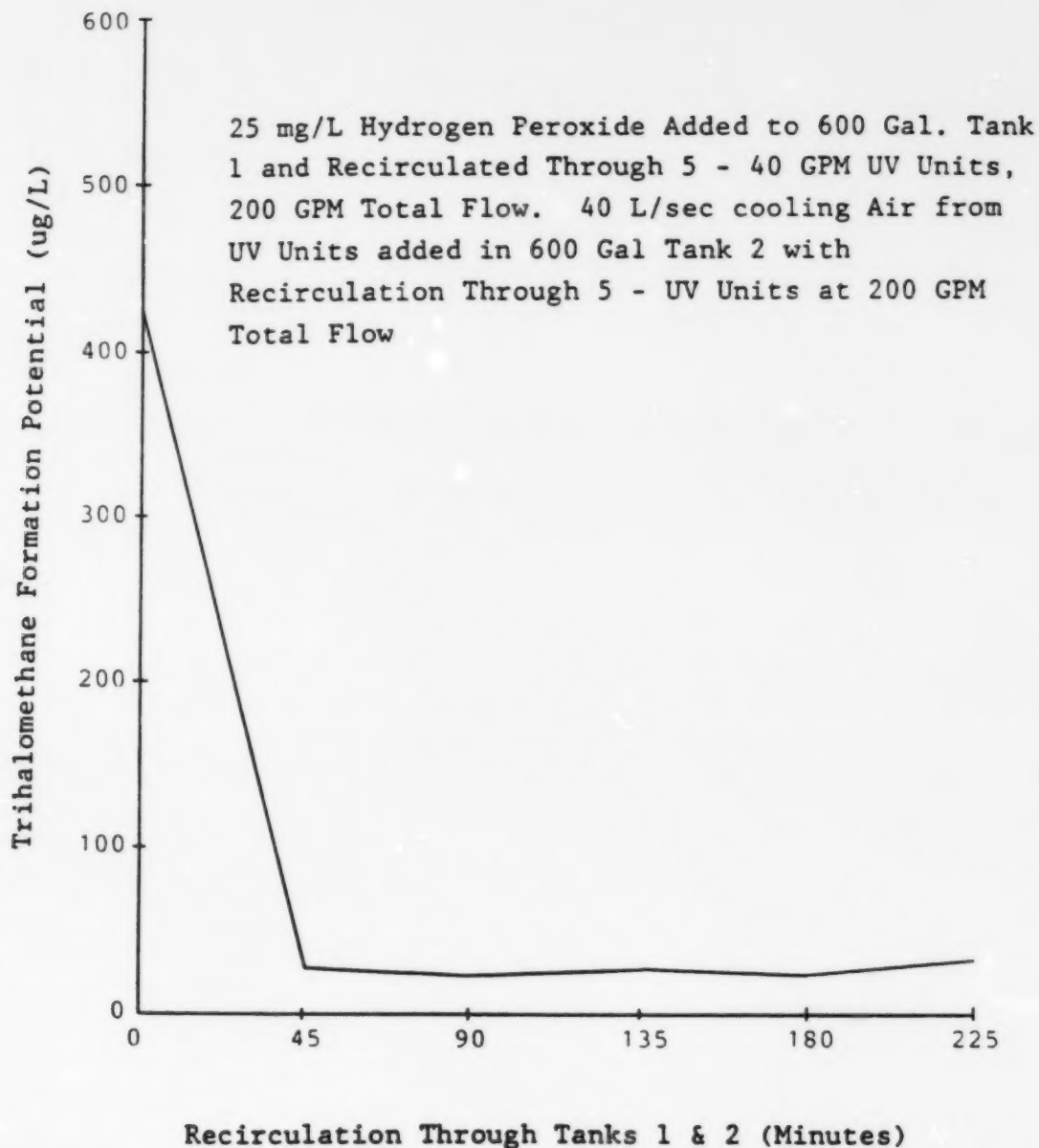


FIGURE 3: Pilot Plant Batch Test of Trihalomethane Formation Potential Reduction.

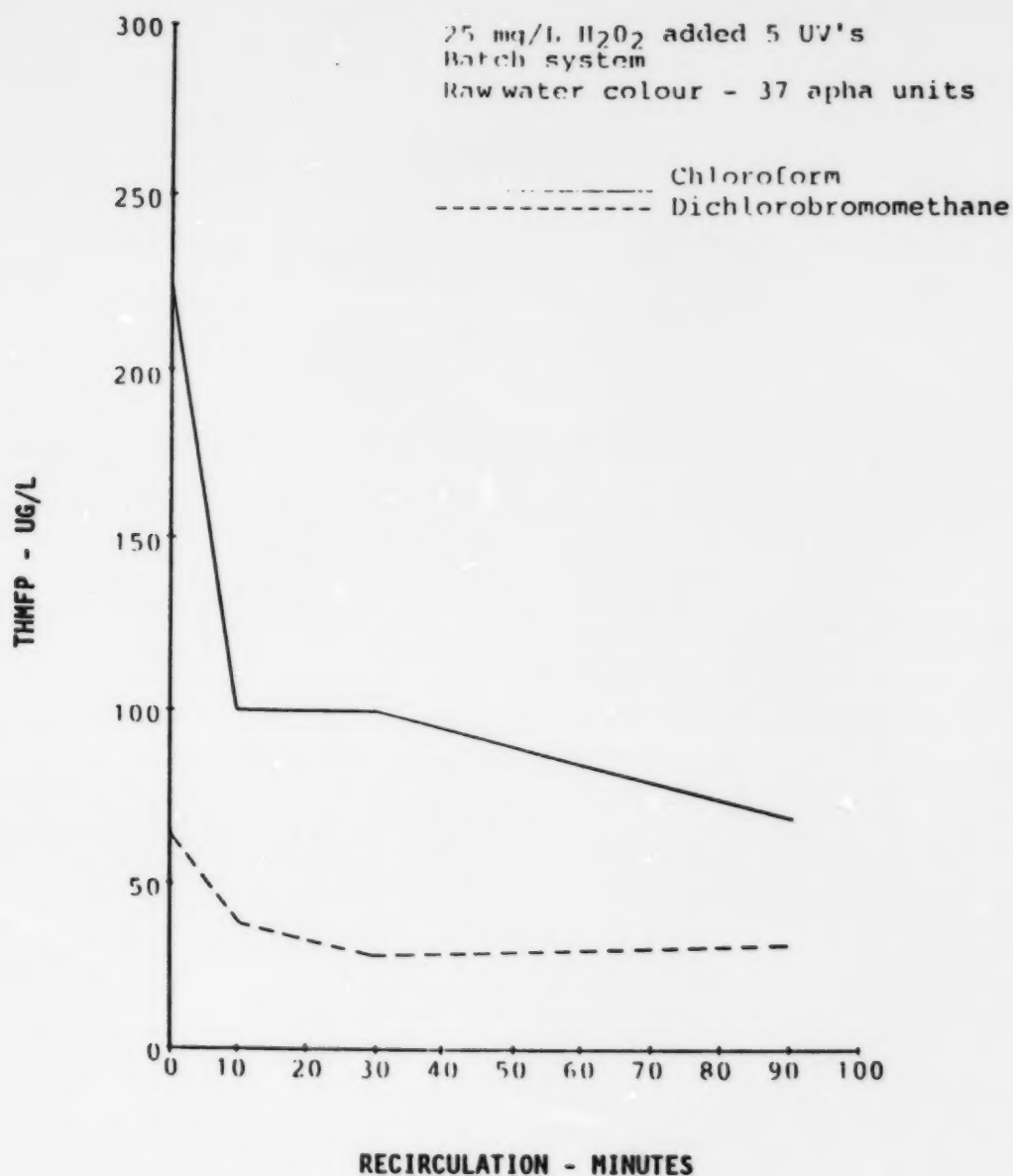


FIGURE 4: Pilot Plant Batch Test of Trihalomethane Formation Potential Reduction Indicating Reduction in Chloroform and Dichlorobromomethane.

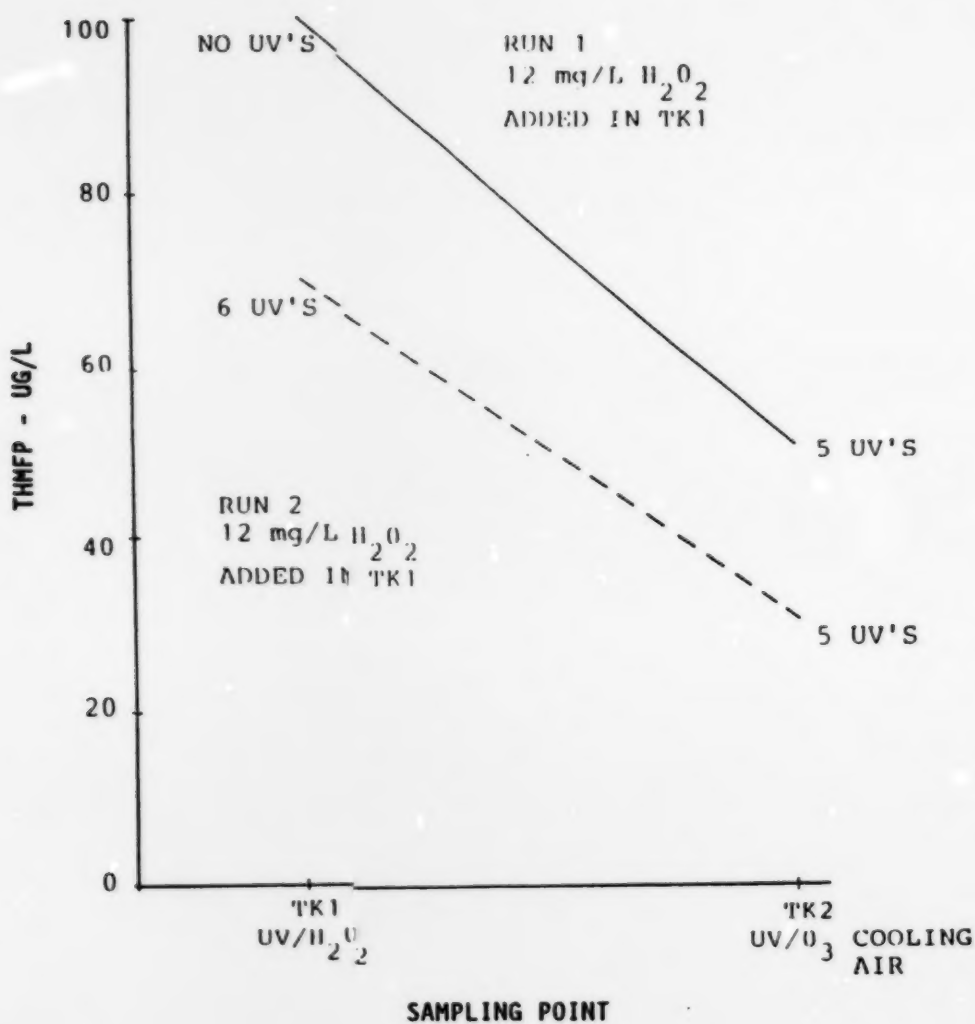


FIGURE 5: Pilot Plant Continuous Flow Test of Trihalomethane Potential Reduction With and Without Ultraviolet Irradiation at Throughput of 21 US GPM.

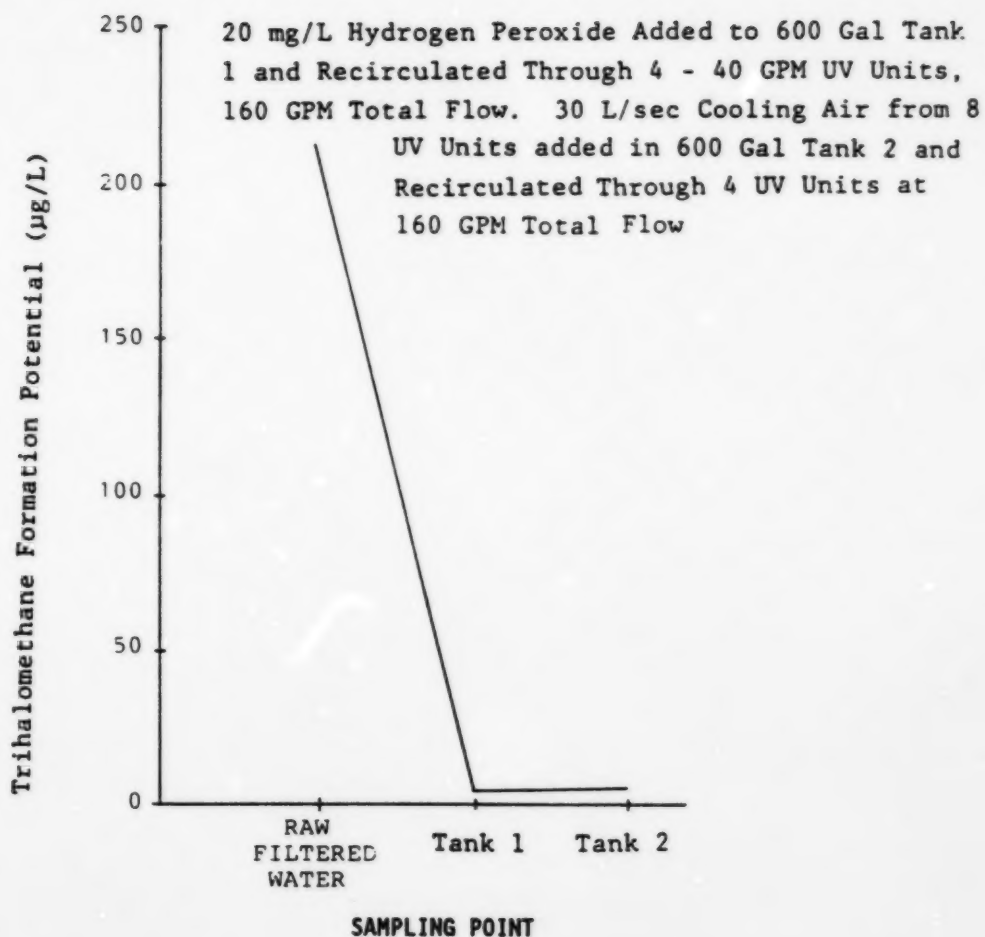


FIGURE 6: Pilot Plant Continuous Flow Test of Trihalomethane Potential Reduction at Throughput of 20 US GPM.

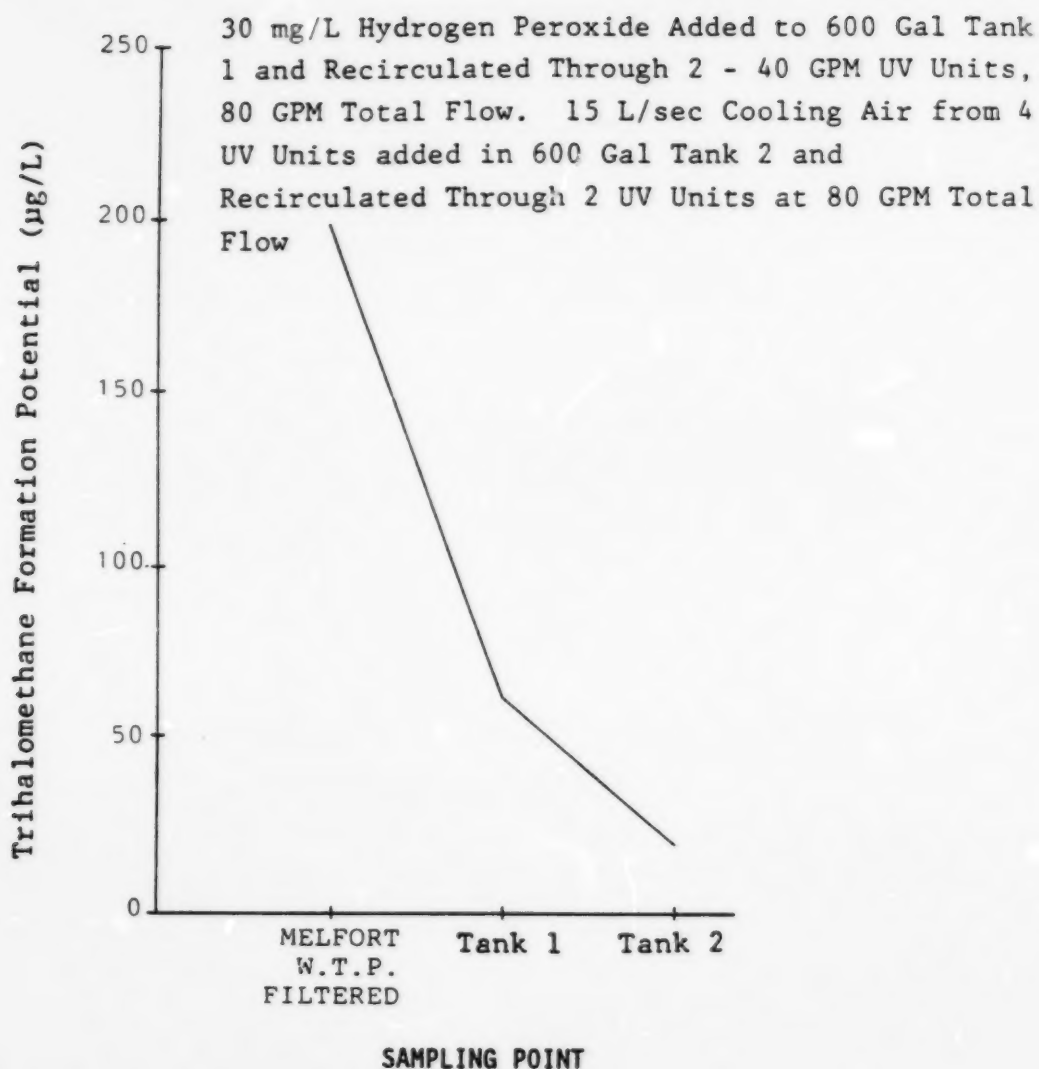


FIGURE 7: Pilot Plant Continuous Flow Test of Trihalomethane Potential Reduction with 20 mg/L Hydrogen Peroxide at Throughput of 20 US GPM.

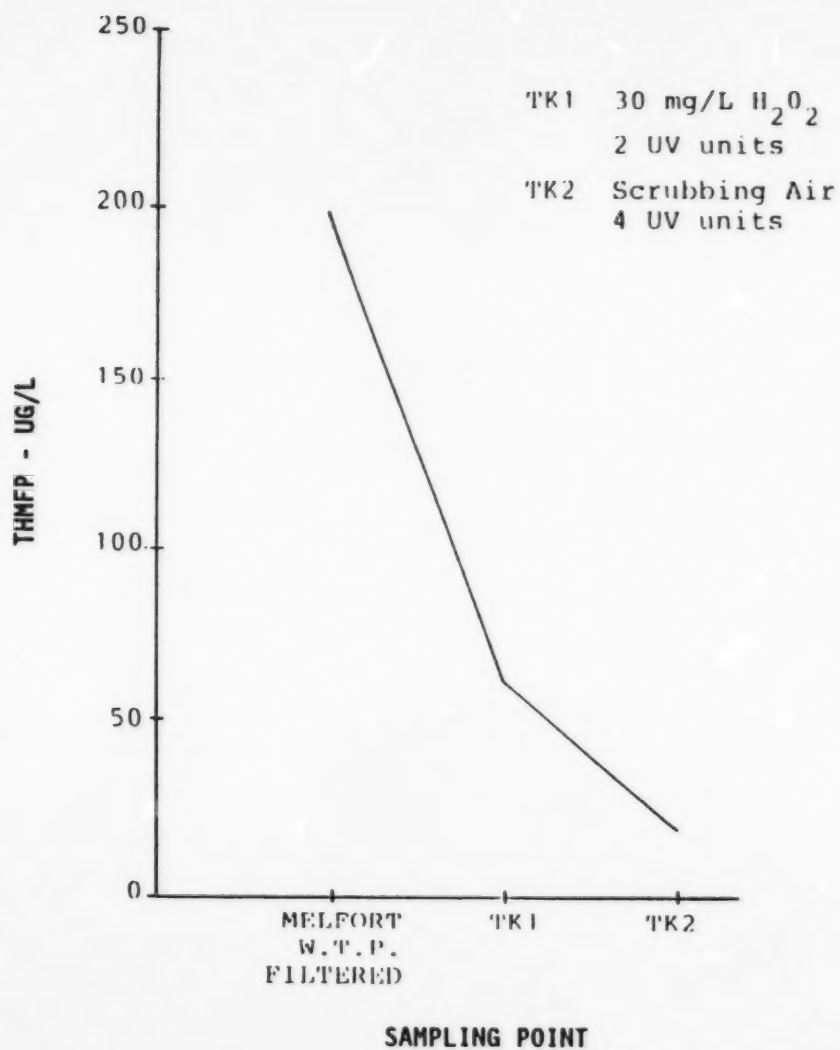
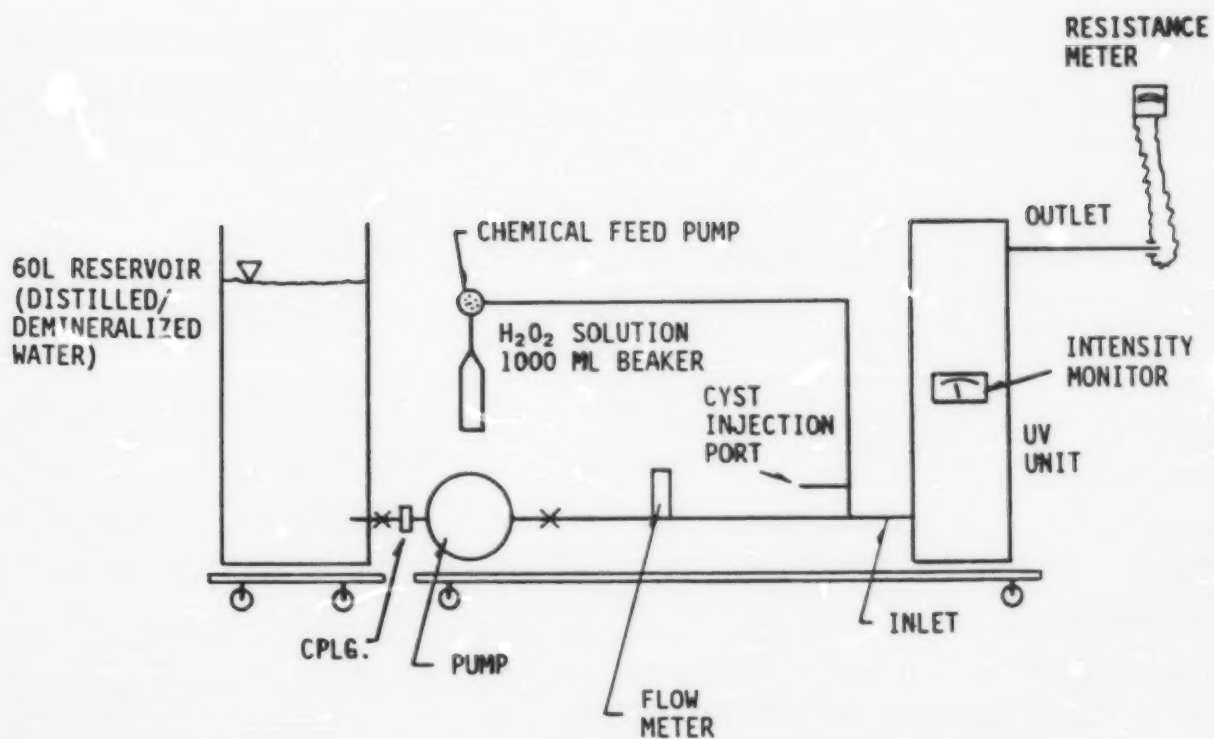
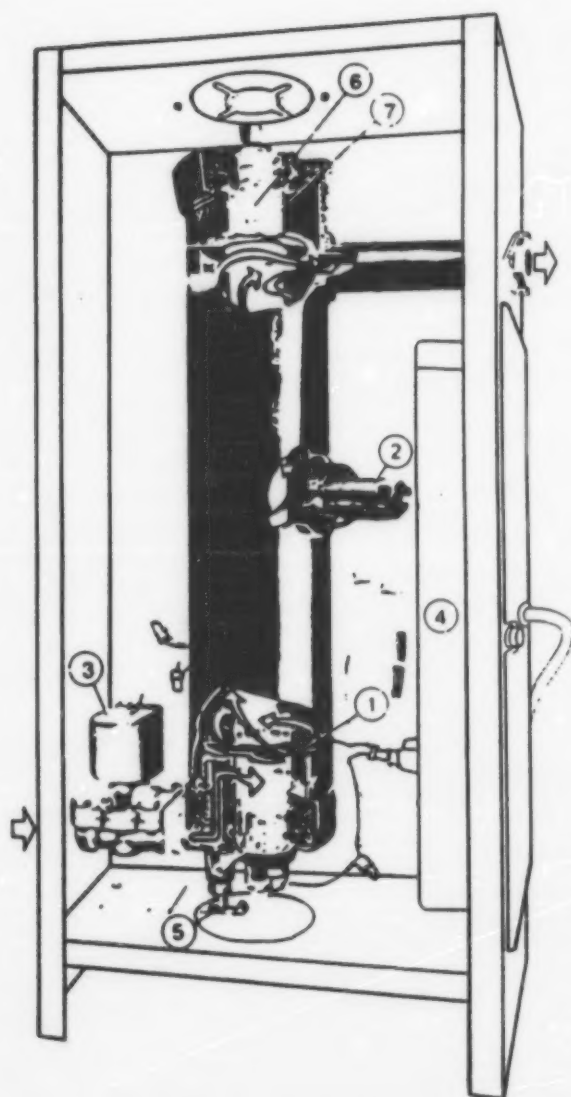


FIGURE 8: Pilot Plant Continuous Flow Test of Trihalomethane Potential Reduction with 30 mg/L Hydrogen Peroxide at Throughput of 20 US GPM.



RESERVOIR & UV SECTION CASTOR MOUNTED

FIGURE 9: UVOX Test Apparatus for *Giardia muris* Cyst Inactivation (Schematic).



1. diffuser plate
2. electronic sensor
3. automatic sheath cleaner
4. solenoid shut-off valve
5. electronic pak
6. drain lock
7. UV light fixture

Model NPS #3 Manufactured by Universal Water
Systems Inc. Vancouver, BC

FIGURE 10: Ultraviolet Disinfection Equipment for UVOX
Giardia muris Cyst Inactivation.

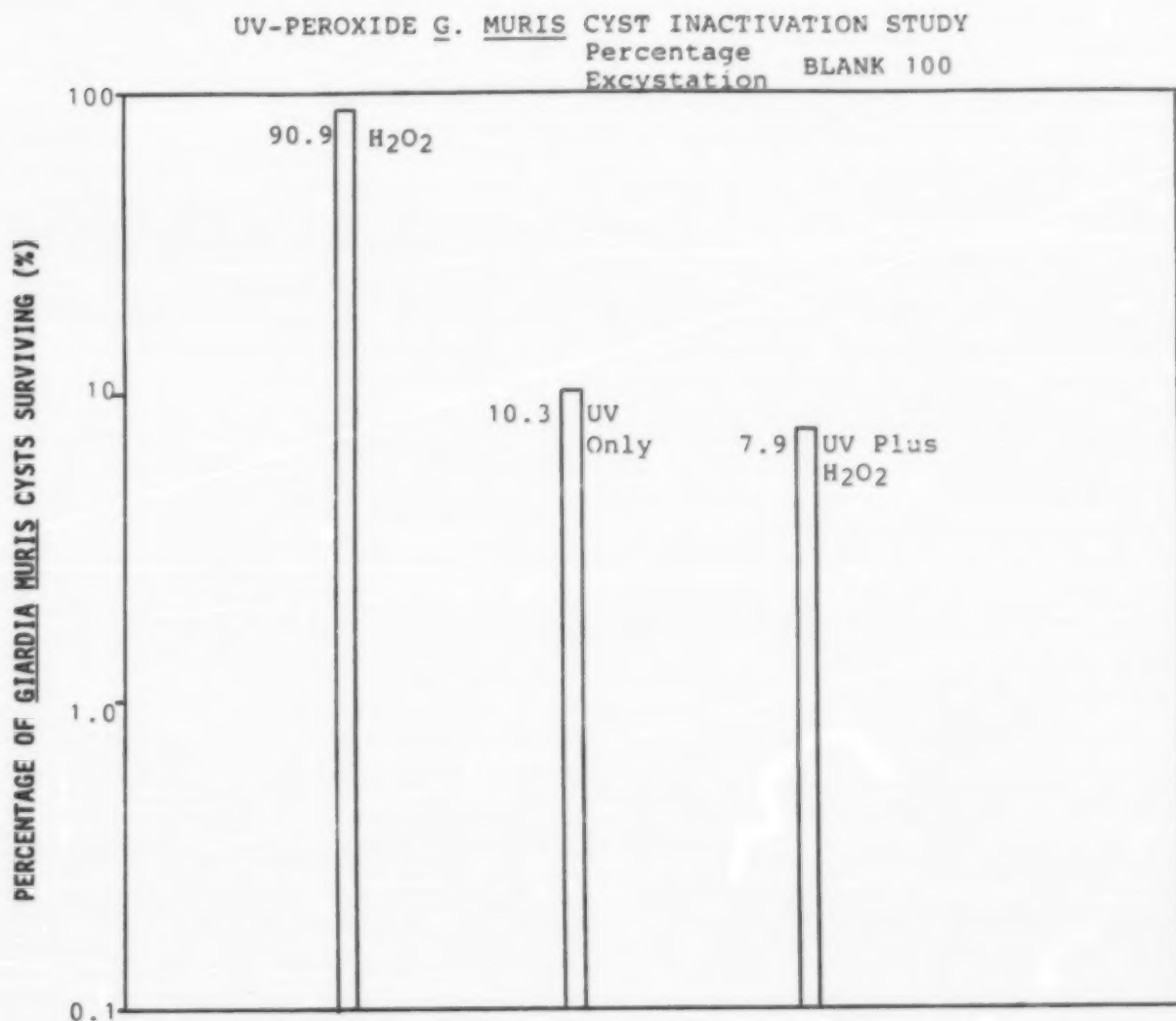


FIGURE 11: *Giardia muris* Cyst Survival with Ultraviolet Dosage of 140 000 $\mu\text{Ws}/\text{cm}^2$ plus 10 mg/L Hydrogen Peroxide.

UV-PEROXIDE *G. MURIS* CYST INACTIVATION STUDY
 Percentage BLANK 100
 Excystation

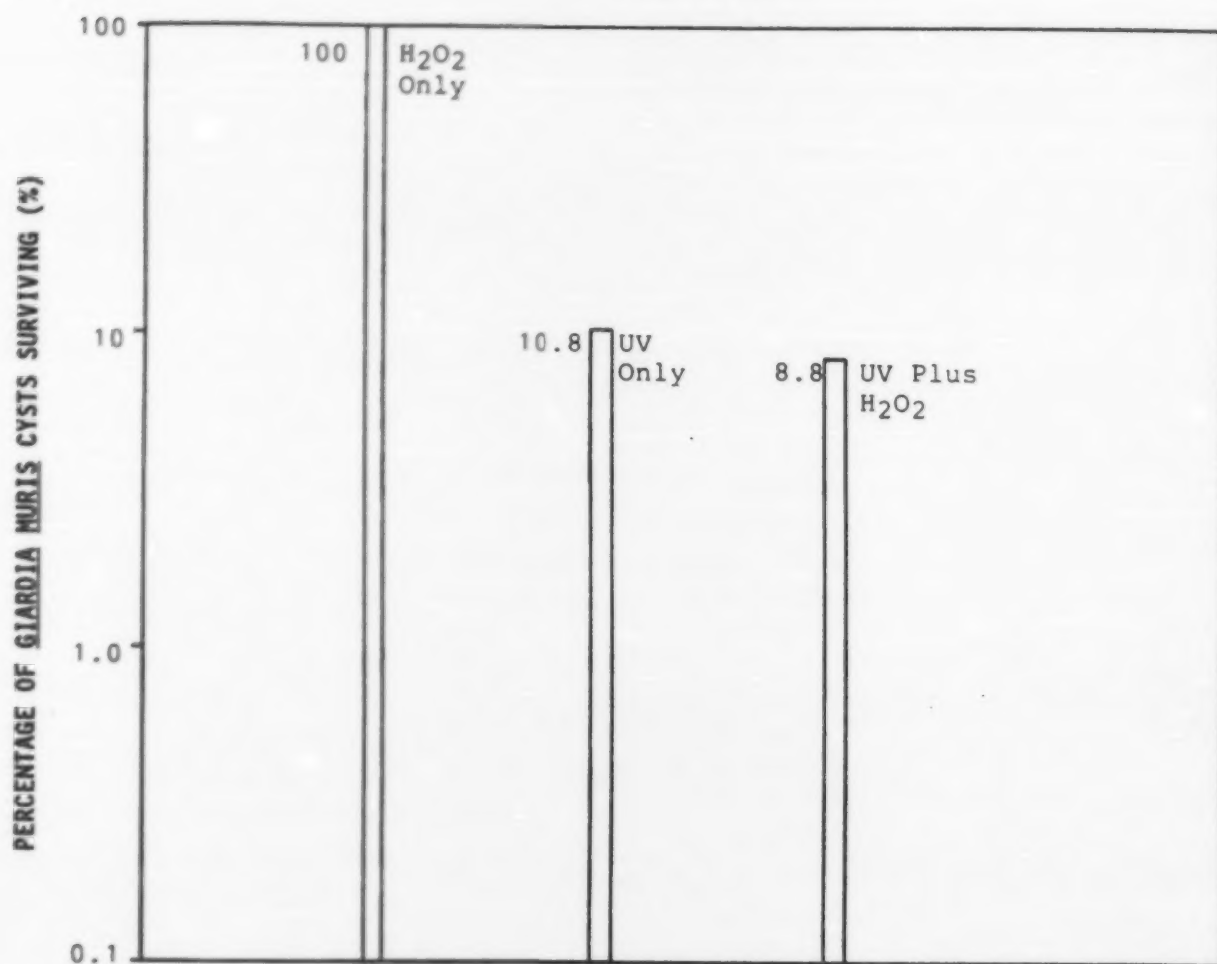


FIGURE 12: *Giardia muris* Cyst Survival with Ultraviolet Dosage of 140 000 $\mu\text{Ws}/\text{cm}^2$ plus 20 mg/L Hydrogen Peroxide.

UV-PEROXIDE G. MURIS CYST INACTIVATION STUDY
 Percentage
 Excystation BLANK 100

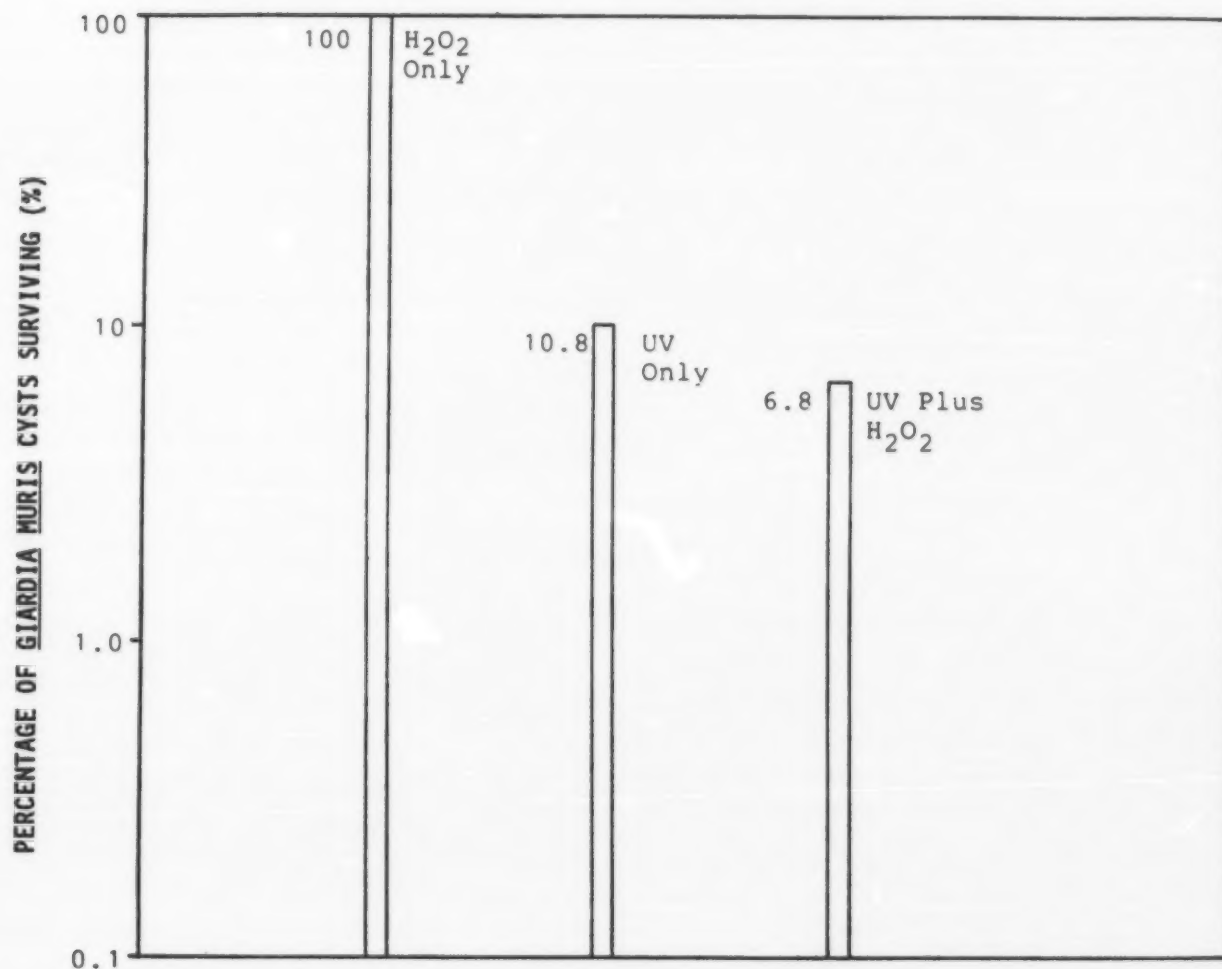


FIGURE 13: *Giardia muris* Cyst Survival with Ultraviolet Dosage of 140 000 $\mu\text{Ws}/\text{cm}^2$ plus 30 mg/L Hydrogen Peroxide.

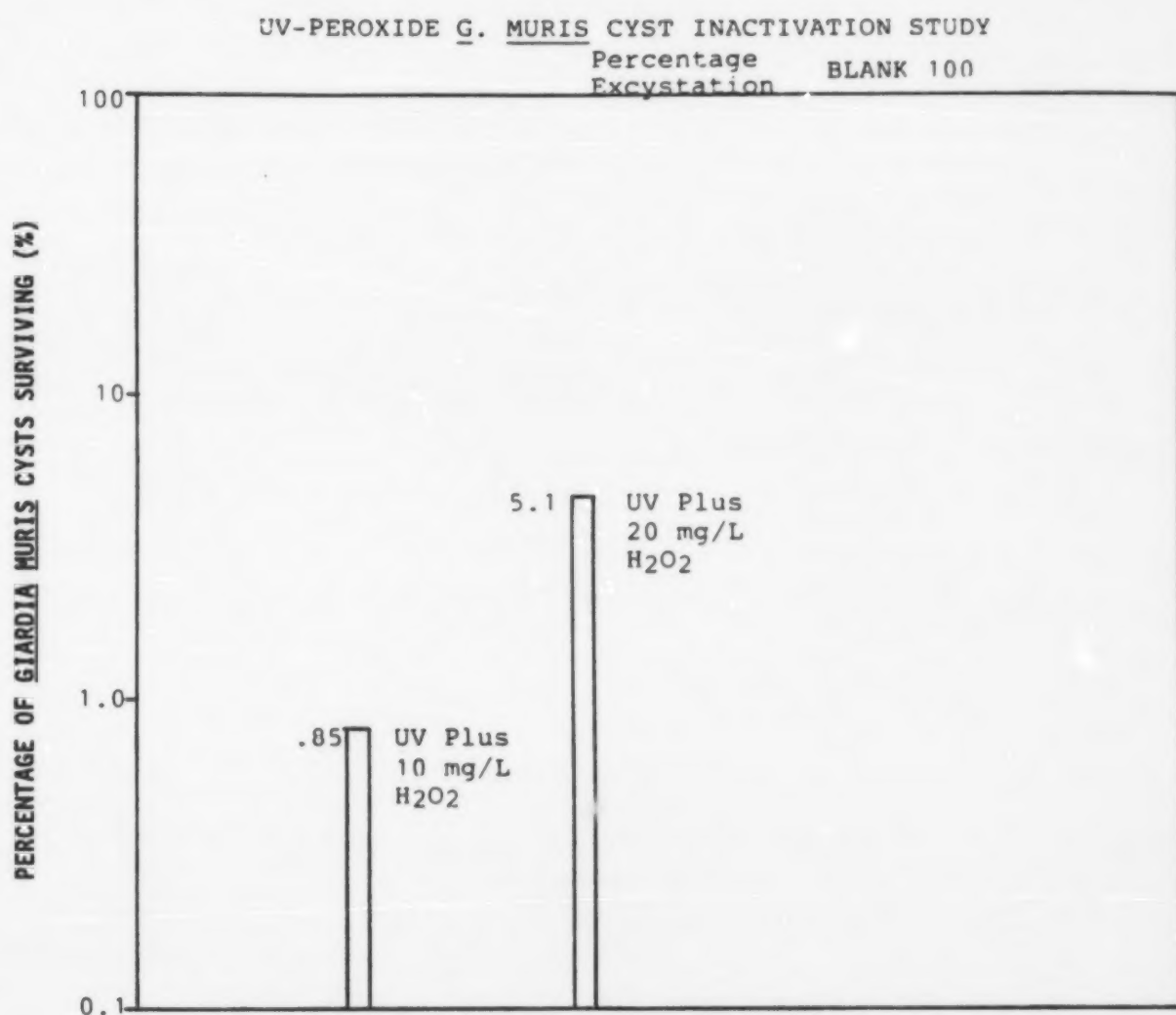


FIGURE 15: *Giardia muris* Cyst Survival with Ultraviolet Dosage of 139 000 $\mu\text{Ws}/\text{cm}^2$ plus 10 and 20 mg/L Hydrogen Peroxide and "Catalase" Bacteria.

UV-PEROXIDE G. MURIS CYST INACTIVATION STUDY
 Percentage
 Excystation BLANK 100

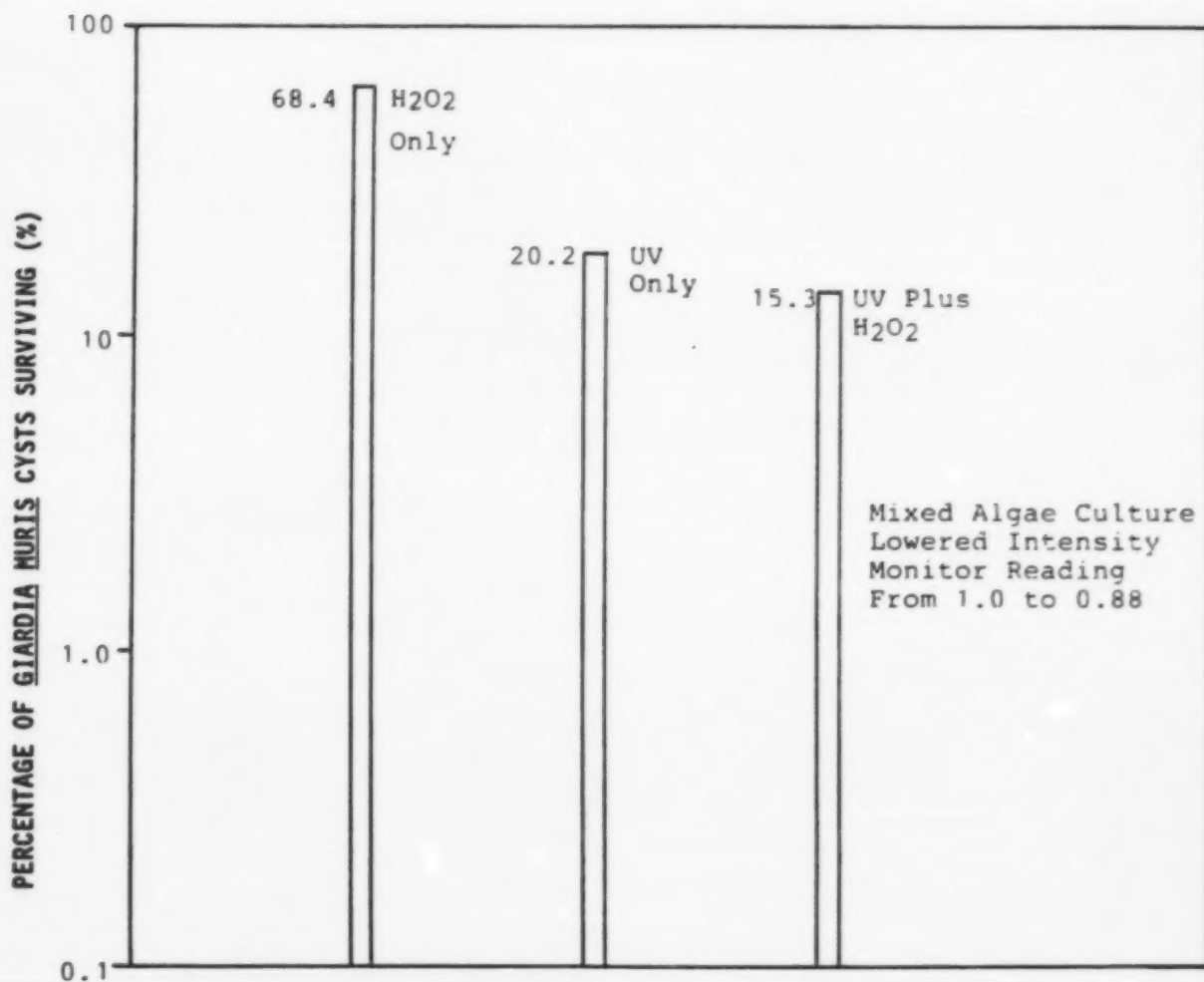


FIGURE 14: *Giardia muris* Cyst Survival with Ultraviolet Dosage of 139 000 $\mu\text{Ws}/\text{cm}^2$ plus 20 mg/L Hydrogen Peroxide and a Mixed Algae Culture.

UV-PEROXIDE G. MURIS CYST INACTIVATION STUDY
 Percentage
 Excystation BLANK 100

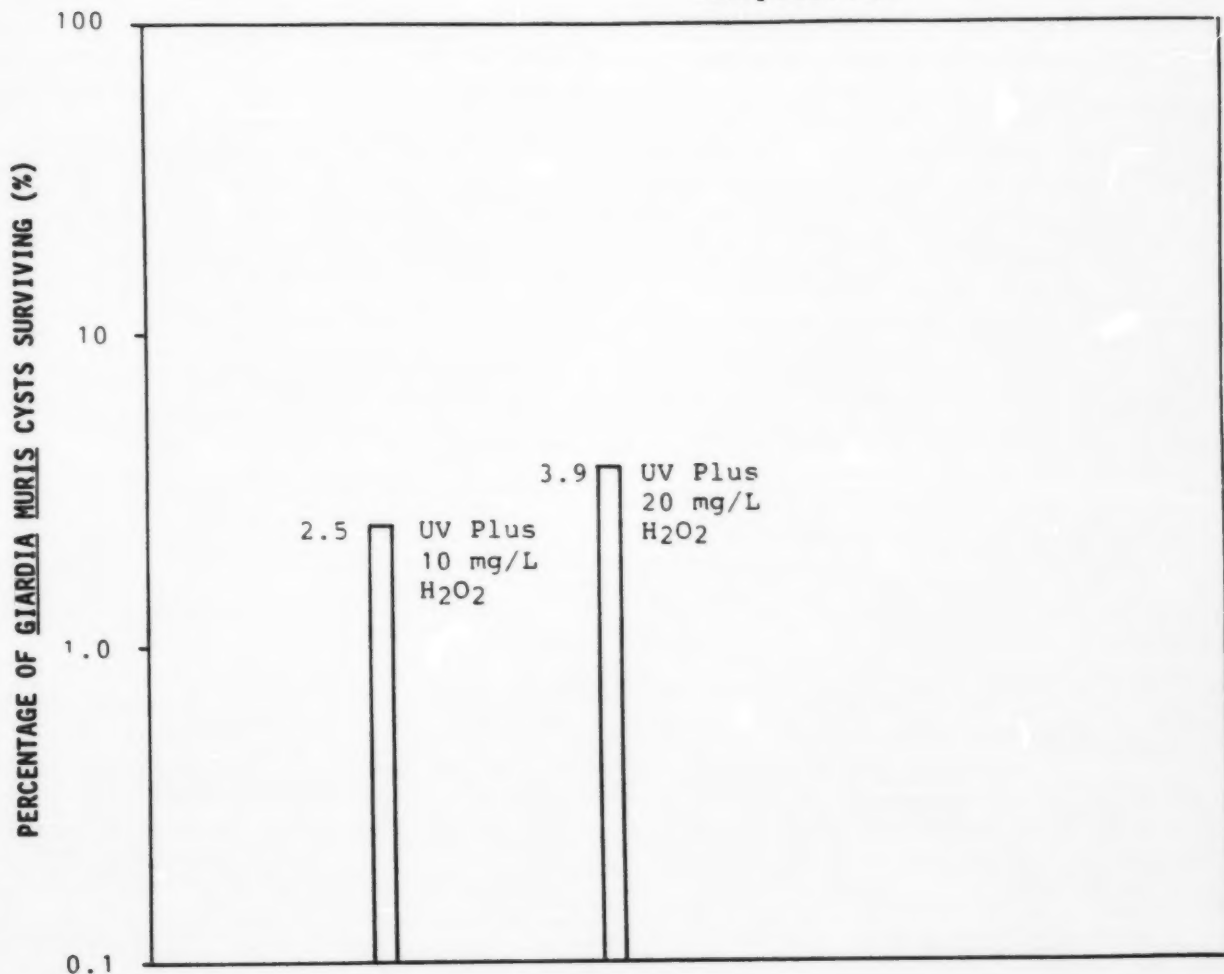


FIGURE 16: *Giardia muris* Cyst Survival with Ultraviolet Dosage of 139 000 $\mu\text{Ws}/\text{cm}^2$ plus 10 and 20 mg/L Hydrogen Peroxide and "Catalase" Bacteria which had been in Contact with Hydrogen Peroxide for 15 Minutes Prior to Irradiation.